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Report No. SFIM-AEC-ETD-CR-95048
FINAL REPORT

Treatment of Propellant Production Wastewaters Containing 2,4-Dinitrotoluene

May 1996
Contract No. DACA31-91-D-0074
Task Order No. 0004

19960705 050

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U.S. Army Environmental Center
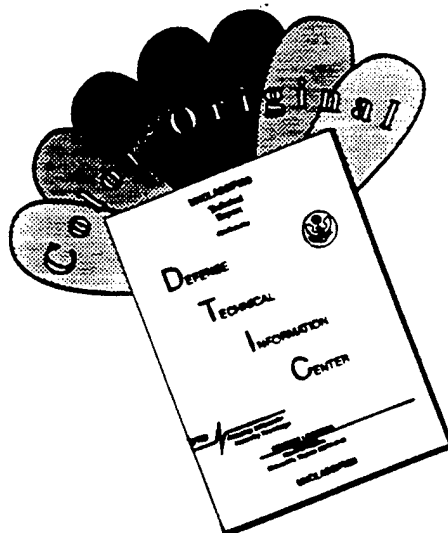Aberdeen Proving Ground, MD 21010-5401

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 31, 1996	3. REPORT TYPE AND DATES COVERED Final Report, 7/93 – 5/96

4. TITLE AND SUBTITLE

Treatment of Propellant Production Wastewater Containing 2,4-Dinitrotoluene

5. FUNDING NUMBERS

6. AUTHOR(S)

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8. PERFORMING ORGANIZATION REPORT NUMBER

322245

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

USAEC
SFIM-AEC-ETD
Aberdeen Proving Ground, MD 21010

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

CR-95048

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unlimited distribution

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The Environmental Technology Division (ETD) of the U. S. Army Environmental Center (USAEC) conducts research and development to support environmental compliance at Army ammunition plants, arsenals, depots, and other Army industrial facilities. Recently, changes in production levels at the Radford Army Ammunition Plant (RAAP), coupled with increasingly more stringent regulation of wastewater discharges, have resulted in the need for improved treatment of propellant production wastewaters containing 2,4-dinitrotoluene (2,4-DNT). The USAEC has supported the evaluation, development, and demonstration of treatment technologies that could enhance RAAP's ability to meet discharge requirements without adversely impacting production capabilities. This report documents the results of pilot-scale demonstrations of two technologies, advanced oxidation and anaerobic fluidized-bed activated-carbon reactors (AnFBR), which were conducted by the USAEC at RAAP. Additionally, a third technology, granular activated carbon (GAC) treatment, was demonstrated at RAAP by Alliant TechSystems. Information regarding GAC is included to facilitate comparisons of the three systems tested.

14. SUBJECT TERMS

2,4-DNT, UV/Oxidation, AnFBR, RAAP

15. NUMBER OF PAGES

138

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

Report No. SFIM-AEC-ETD-CR-95048

FINAL REPORT

TREATMENT OF PROPELLANT PRODUCTION WASTEWATER CONTAINING 2,4-DINITROTOLUENE

May 1996
Contract No. DACA31-91-D-0074
Task Order No. 4

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U.S. Army Environmental Center
Aberdeen Proving Ground, MD 21010-5401

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LIST OF ACRONYMS

2,4-DNT	2,4-Dinitrotoluene
ACO	Administrative Contracting Office
AnBSR	Anaerobic Biological Reactor with Synthetic Resin
AnFBR	Anaerobic Fluidized-Bed Biological Reactor
AOP	Advanced oxidation process
BWTP	Biological Wastewater Treatment Plant
COD	Chemical Oxygen Demand
2,4-DAT	2,4-Diaminotoluene
2,4-DNT	2,4-Dinitrotoluene
DO	Dissolved Oxygen
ETD	Environmental Technology Division
GAC	Granular Activated Carbon
GOCO	Government Owned Company Operated
gpd	gallons per day
gpm	gallons per minute
IRGA	Infra Red Gas Analyzer
kWh	kilowatt hours
MSDS	Material Safety Data sheets
nm	Nanometer
NTU	Nephelometric Turbidity Unit
OLR	Organic Loading Rate

ORP	Oxidation-Reduction Potential
PLC	Programmable Logic Controller
POTW	Publicly Owned Treatment Works
psi	per square inch
ppm	parts per million
RAAP	Radford Army Ammunition Plant
RBC	Rotating Biological Contactors
RCRA	Resource Conservation and Recovery Act
SBR	Sequencing Batch Reactor
TNT	Trinitrotoluene
TSS	Total Suspended Solids
UOP	Unit Operating Procedure
USACERL	U.S. Army Construction Engineering Research Laboratory
USAEC	U.S. Army Environmental Center
USEPA	U.S. Environmental Protection Agency
UV/OX	Ultraviolet/ Oxidation
VFA	Volatile Fatty Acids

ACKNOWLEDGMENT

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1.0 INTRODUCTION

The Environmental Technology Division (ETD) of the U.S. Army Environmental Center (USAEC) conducts research and development to support environmental compliance at Army ammunition plants, arsenals, depots, and other Army industrial facilities. Recently, changes in production levels at the Radford Army Ammunition Plant (RAAP) coupled with increasingly stringent regulation of wastewater discharges, have resulted in the need for improved treatment of propellant production wastewaters containing 2,4-dinitrotoluene (2,4-DNT). The USAEC has supported the evaluation, development, and demonstration of treatment technologies that could enhance RAAP's ability to meet discharge requirements without adversely impacting production capabilities. This report documents the results of pilot-scale demonstrations of two technologies, advanced oxidation and anaerobic fluidized-bed biological reactor (AnFBR) with granular activated carbon followed by a Rotating Biological Contactor (RBC), which were conducted by the USAEC at RAAP. Additionally, a third technology, granular activated carbon (GAC) treatment was demonstrated at RAAP by Alliant Techsystems. Information regarding GAC is included to facilitate comparisons of the three systems tested.

1.1 Background

RAAP is located in a rural setting in southwest Virginia near Radford. It is a government owned, contractor operated (GOCO) facility currently operated by Alliant Techsystems, Inc. (formerly Hercules Aerospace Division). The RAAP produces a wide variety of propellants and explosives for use by the U.S. military. 2,4-DNT is used in the production of single-base propellants (e.g., M-14) as a plasticizer, to reduce hygroscopicity, as a deterrent surface coating, improve mechanical properties, alter thermochemistry and burning rate, and facilitate solvent removal.[1] The propellants contain 3 to 10 percent 2,4-DNT by weight. Production of single-base propellants at RAAP is conducted as a batch mode process that includes operations which generate wastewater (i.e., solvent recovery, water-dry, and wet screening). (A more detailed description of the manufacturing process is presented in Section 2.0.) These wastewaters contain various concentrations of 2,4-DNT and other organics (e.g., ethanol and ether) and are discharged to the industrial sewer. An on-site biological wastewater treatment plant (BWTP)

treats the combined flow of wastewater from most on-site production operations. The treated effluent is discharged from the BWTP to the New River which flows through the facility.

This discharge is regulated by the Commonwealth of Virginia under a National Pollutant Discharge Elimination System (NPDES) permit. It is anticipated that the state will significantly reduce the NPDES discharge limit for 2,4-DNT. Currently the daily discharge limits for 2,4-DNT are 113 µg/L (average concentration) and 285 µg/L (maximum concentration). In the past, the BWTP has occasionally discharged treated effluent that exceeded these concentrations but were within Virginia Water Quality Standards quantity limits for DNT in public water supplies based on the harmonic mean flow of the New River.

To support RAAP's efforts to address this situation, the USAEC sponsored an engineering study to identify the major sources of 2,4-DNT present in wastewater generated at RAAP and to characterize the flows and concentrations of these wastewaters.[2] Limited bench-scale testing of selected treatment technologies was also conducted during this initial study. It was concluded that approximately 75 percent of the 2,4-DNT bearing wastewater originates from propellant manufacturing, specifically from the water-dry process. In this process, solvents and 2,4-DNT are leached from the solid propellant as it steeps in hot water. In addition to 2,4-DNT, ethanol and ether are present in significant concentrations in the water-dry effluent. The wet screening operations and solvent recovery operations were estimated to contribute approximately 18 and 7 percent, respectively, of the 2,4-DNT load to the BWTP.[2]

Based on the results of the preliminary study, it was concluded that interception and pretreatment of the water-dry wastewater at a point upstream of the BWTP was an option that could significantly reduce the 2,4-DNT load to the BWTP. It was further concluded, as a result of the USAEC's previous evaluations, that granular activated carbon (GAC), ultraviolet oxidation (UV/OX), and biodegradation technologies potentially could be effective in this application for the treatment of 2,4-DNT and that additional evaluation and pilot-scale demonstrations were warranted.

Subsequent to the USAEC's initial evaluations, the U.S. Army Construction Engineering Research Laboratory (USACERL) investigated the feasibility of using anaerobic fluidized-bed biological reactor (AnFBR) with granular activated carbon technology for treatment of wastewater containing 2,4-DNT.[3] During this evaluation, a bench-scale treatability study was conducted using both simulated wastewater (i.e., a laboratory prepared surrogate) and actual water-dry wastewater generated at RAAP. This technology development and evaluation confirmed that AnFBR technology offered favorable prospects for treatment of water-dry wastewater. It was noted that the bio-transformation product of anaerobic degradation of 2,4-DNT was 2,4-Diaminotoluene (2,4-DAT).[2,3]

The current USAEC project included a review of available information to confirm that UV/OX and AnFBR technologies were appropriate selections for pilot-scale demonstration. The information acquisition and technology demonstrations were intended to support design of a full-scale system if either or both technologies were proven at pilot-scale. During the literature search to identify technologies capable of treating or removing 2,4-DNT in wastewaters, successful treatment of 2,4-DNT or an analogous compound, at bench-, pilot-, or full-scale, was the minimum criterion necessary for further consideration of a technology. The literature search identified six technologies, including UV/OX and AnFBR, as candidates for further evaluation. Preliminary budgetary cost estimates for full-scale systems were prepared based on estimated flow rates of water-dry wastewater and concentrations of 2,4-DNT documented in the previous USAEC and USACERL studies. Evaluation of the candidate technologies resulted in the decision to conduct pilot-scale demonstrations of both UV/OX and AnFBR technologies. Additional details of the technology selection process are presented in Section 3.

1.2 Scope and Objectives

The scope of the current study focused on conducting on-site, pilot-scale demonstrations of UV/OX and AnFBR technologies. Specific objectives included demonstrating whether these technologies were capable of removing or destroying 2,4-DNT while meeting site safety and environmental requirements. Performance data was collected under actual field conditions to allow realistic and comparative assessments of the technologies. Further, the on-site

demonstrations were to provide information that would support design of a full-scale system for the selected alternative.

Several parties were involved in the demonstrations. The scope and objectives of the overall effort were divided among the participants whose activities were directed by the USAEC. Under contract to the USAEC, IT Corporation reviewed available information and recommended technologies for testing, prepared the documents necessary for the tests (i.e., Health and Safety Plan, the Test Plan, and the Site Safety Submission), prepared bid specifications and procured the UV/OX system (on a short term rental basis), provided coordination and technical oversight during the demonstrations, and prepared technical reports. Under a separate contract to the USAEC, Alliant prepared and provided the test site, provided operators for installation, operation, and demobilization of the test equipment, and provided the on-site analytical services. In support of the USAEC's demonstration program, USACERL provided technical expertise and review throughout the planning and execution of the demonstrations. Additionally, USACERL provided the AnFBR test unit. The AnFBR system was manufactured by Envirex, Inc. and procured by EFX Systems, Inc. (EFX) (formerly a part of the Michigan Biotechnology Institute, MBI) under a separate contract to USACERL. EFX also provided technical support and assistance during operation and testing of the AnFBR system. The U.S. Army's Administrative Contracting Office (ACO) at RAAP provided site access and coordination of efforts regarding compliance with environmental regulations and site specific requirements.

IT's scope of work included preparation of the following documents during the course of the project to support the demonstrations:

Test Plan for Treatment of Propellant Production Wastewater - This document specified the procedures to be followed in conducting the demonstration. It included an overview of the test program, provided descriptions of the equipment, and identified the parameters of concern. The Test Plan also included the sample locations, sampling frequency and protocols, and analytical methods. The Test Plan was based on information provided by Alliant, the equipment vendors, and EFX.

Health and Safety Plan - This document was prepared for use by all on-site personnel while performing the demonstrations. The document identified the hazards likely to be encountered, specified the protective clothing to be worn by the operators, defined personnel monitoring requirements, and included material safety data sheets (MSDS) for all chemicals used during the demonstrations, and other relevant and required safety requirements.

Site Safety Submission - The submittal of this document was a site requirement prior to the start of any work in an explosive manufacturing area of the plant or any work involving propellants (including water-dry wastewater). The document specified the location of the work, the intraline distances to surrounding buildings and roadways, the fire and explosive potential of the materials under consideration and in adjoining buildings, the maximum storage quantity of materials in the test building and adjoining buildings, and any site modifications to existing structures that were necessary. The document was prepared jointly by IT and Alliant.

Hazards Analyses - All equipment used at RAAP was subjected to an analyses of the potential hazards associated with its operation in accordance with Army and Alliant safety standards. The hazards analysis included examination of electrical hazards, toxicity of the chemicals to be used, gases likely to the produced, explosive potential, and other operational concerns. The hazards analysis was performed by Alliant with information and support provided by IT and the equipment vendors.

Unit Operating Procedures (UOPs) - In accordance with Alliant safety standards, UOPs that provide detailed instructions to operators for operating equipment were prepared. Separate UOPs were prepared for filling the 20,000 gallon tank with WD wastewater, operating the UV/OX system, and operating the AnFBR/RBC systems. The UOPs were prepared jointly by IT and Alliant. A copy of the UOPs were included in the Test Plan as an appendix.

1.3 Report Organization

Section 2 of this document presents background information on the site and wastewaters containing 2,4-DNT. This section also includes descriptions of the propellant manufacturing process and the facilities used for these demonstrations. A review of the technology selection

process used for this pilot-scale demonstration is presented in Section 3. Sections 4, 5, and 6 provide discussions of the UV/OX, AnFBR, and GAC demonstration programs, respectively. An evaluation, including cost comparisons of the alternatives for treatment of DNT-bearing wastewater, is presented in Section 7. Conclusions are presented in Section 8 and references cited in this report are listed in Section 9.

2.0 SITE DESCRIPTION

The RAAP is an expansive production facility that manufactures a wide variety of propellants and explosives for the U.S. military. The site description presented in this section is limited to the production of single-base propellants. Specifically, the discussion focuses on the major production operations that generate aqueous effluents that are contaminated with 2,4-DNT (i.e., solvent recovery, water-dry, and wet screening operations). A description of the facilities used for the pilot-scale demonstration is also presented.

2.1 Propellant Manufacturing Operations at RAAP

The current annual production rate of single-base propellants at RAAP is approximately 3.5 to 4.0 million pounds. It is anticipated that this rate of production will be sustained over the near term (i.e., 3 to 5 years). However, production levels are dependent upon DoD requirements and fluctuate with changing military requirements. Single-base propellants (e.g., M-14 for M865, M490A1, and M831A1; M6+2 for 76mm; M1MP for M724A1 and M67) are manufactured in batch mode operations that consist of several sequential process steps. During production, each batch of propellant is physically transferred between the buildings that are used for each step of the operation. A generalized process flow chart of the manufacturing process for single-base propellants containing 2,4-DNT is presented in Figure 2-1. The starting material (base) for propellant manufacture is nitrocellulose. The nitrocellulose, which is produced on-site, is first dewatered by centrifugal action in a Wringer House and then by solvent extraction in a dehydration press building. Neat 2,4-DNT, procured from an outside source, is sized by screening and weighed at the DNT Screen House for subsequent mixing with the nitrocellulose and other propellant ingredients and solvents (alcohol and ether) at the Mix Houses. After mixing, the material is pressed into blocks which are then extruded through screens and dies (block and macaroni presses) to remove unplasticized material. The material is then extruded through dies and cut to the desired configuration in the Press and Cutting House. Inert gas is utilized to extract and recover alcohol and ether, which are processing solvents, in the Solvent Recovery (SR) process. After solvent recovery, remaining residual solvents are removed by steeping the propellant in hot water in the Water-Dry (WD) Buildings. From the WD process,
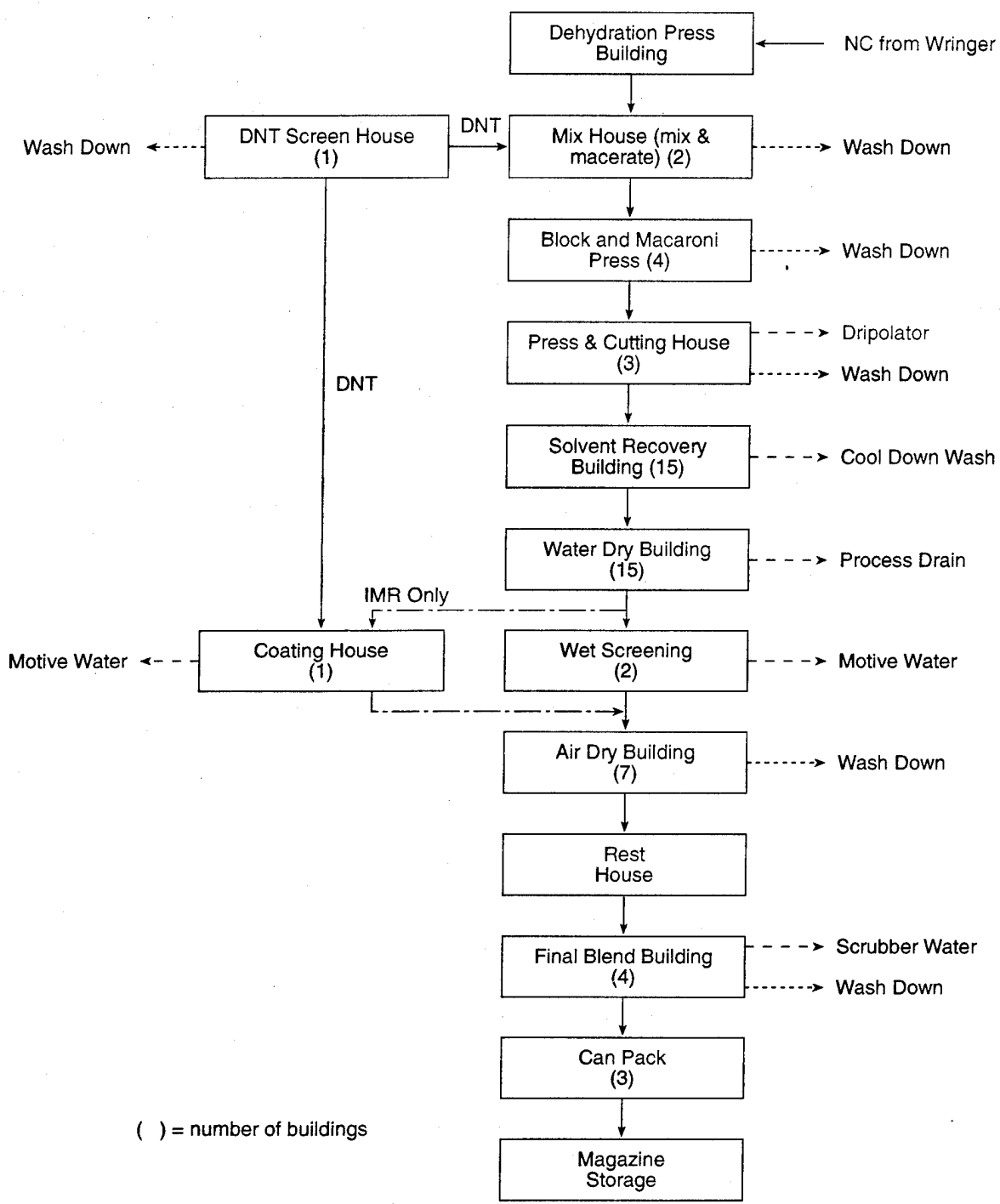
Figure 2-1.
Production of Propellant
Containing DNT.

the batch of propellant is transferred to Wet Screening (WS) where any agglomerations are broken apart and any undersized (i.e., off-spec size) grains are removed. The propellant is then air dried (AD) to reduce its moisture content. The final production operations involve packout of the material. Additionally, the specifications for some propellants require that a coating of 2,4-DNT be applied, this is performed in the Coating Operations (CO) buildings.

Processes contributing 2,4-DNT to the industrial wastewater system during these manufacturing operations are indicated in Figure 2-1. Of the wastewater sources identified on the figure, the following four processes are the major contributors of DNT contaminated wastewater: SR (cool down, wash water, and motive water); WD (process water, motive water, leak and overflow water); WS (motive water); and CO (process water). These operations and the effluents generated are described more fully in the following paragraphs.

Each active SR building houses five process tanks. Each tank can hold approximately 10,000 lbs of solvent-rich propellant. After the propellant is placed in the SR tank, it is first exposed to a flow of heated, inert gas which drives off ethyl alcohol (alcohol) and ethyl ether (ether). Following this operation, the propellant is covered with water (approximately 1,250 gallons per building) to remove solvents adhering to the surface and to reduce the electrostatic potential.[2] At the completion of the SR process, approximately 4,000 gallons of water is used per building to transfer the propellant from the tanks to wheeled buggies. During each production cycle, therefore, each SR building generates an estimated 5,250 gallons of wastewater contaminated with 2,4-DNT, alcohol, and ether.[2] This wastewater enters drains in the SR buildings which are connected to the industrial sewer system. The SR effluents combine with other production wastewaters and flow to the BWTP. It has been estimated that the SR process contributes approximately 7 percent of the DNT load to the BWTP.

Propellant is transferred from the SR to the WD buildings where it is loaded into large open-top tanks. During the WD operation, the propellant is steeped in hot water to remove residual solvents primarily ethanol and diethyl ether. Each WD building contains two 20,000-gallon fiberglass wooden stave tanks. Approximately 40,000 lbs of propellant is loaded into each tank and covered with water that is heated to 65°C and recirculated. The propellant is allowed to soak

in the hot water for 4 to 18 days, depending on the propellant formulation and production schedule. The minimum time in WD is 11 days for propellant formulations such as M14. At the completion of the WD cycle (which is determined by analysis of propellant samples by the production quality control laboratory), approximately 7,000 gallons of process water is released from each WD tank as they are drained.[2] An additional 3,000 gallons (approximately) per tank is then required to flush the propellant from the tanks into transport buggies.[2] Thus, each WD building has the potential to contribute approximately 20,000 gallons of wastewater containing 2,4-DNT to the BWTP during an 11-day production cycle. Currently, eight of the 32 WD buildings at RAAP are active, the others have been put into standby status (i.e., they are inactive and not used). The concentration of 2,4-DNT in WD wastewater varies widely. It ranges from <10 to >250 mg/L, an average of 75 mg/L has been used in previous reports.[2] The WD process is the most significant source of DNT in propellant production wastewater at RAAP. It has been estimated that WD contributes about 75 percent of the DNT sent to the BWTP.[2]

From the WD operation the propellant is transferred to one of the WS buildings. It is estimated that the WS operation generates approximately 1,000 gallons of wastewater per WD tank load of propellant.[2] This wastewater contains significantly lower quantities of 2,4-DNT than WD or SR effluents. The coating operations, a finishing step, is estimated to generate between 15,000 and 30,000 gallons of wastewater per year.[2]

It has been previously concluded that the major contributor of 2,4-DNT load to the BWTP is the WD operation. Previous studies recommended interception and treatment of WD wastewater prior to discharge from the WD tanks to the sewer to help ensure that the treated effluent from the BWTP is in compliance with the current and anticipated NPDES discharge limits for 2,4-DNT.

2.2   Biological Wastewater Treatment Plant (BWTP)

Treatment of industrial wastewaters at RAAP is accomplished in an on-site BWTP that consists of an equalization basin, aerobic rotating biological contactors (RBC), and clarifiers to treat the combined waste streams. A major expansion of the BWTP is currently being completed. Although this construction activity will not change the wastewater treatment technology (i.e.,

RBCs will still be used) it will significantly increase the treatment capacity of the BWTP. The capacity of the equalization basin has been significantly increased which will dampen fluctuations in flow and should reduce variations in DNT concentrations in the combined wastewaters. The larger plant will allow operation at significantly longer retention times if desired. A schematic flow diagram of the existing BWTP is presented in Figure 2-2. The combined industrial wastewaters flow to the BWTP and are pumped by a lift station to a concrete, lined, equalization basin (installed and brought online in September 1995). The wastewater is pumped from the equalization basin to six aerobic RBCs, arranged in two parallel rows of three RBCs each. The wastewater exiting the RBCs is combined, and then split again into two clarifiers prior to discharge of treated effluent to the New River via a NPDES permitted outfall. Sludge from the clarifiers is treated in three aerobic digestors, thickened, and dewatered by filter press prior to off-site disposal.

On occasion, the BWTP has experienced difficulty in meeting the effluent limit for 2,4-DNT. This has probably been due, at least in part, to significant fluctuations in the volume and characteristics of the wastewater treated. Additionally, the development of increasingly more sophisticated analytical capabilities have allowed lower detection limits for 2,4-DNT. Fluctuations in wastewater generation have been associated with changes in production levels. The downsizing of military requirements has resulted in lower demand for propellants. Because production at RAAP is largely a batch mode operation, the BWTP has experienced slug loads of the various wastewaters, including WD and other DNT-bearing effluents. Such fluctuations can inhibit efficient operation of a biological based treatment system. If the periods between slug flow events are excessive, the biomass on the RBCs will require a period for reacclimation. During this period, treatment efficiency can be reduced. However, previous studies did not indicate any apparent correlation between the excursions and propellant production levels.[2]

A graph comparing 2,4-DNT concentrations in the BWTP influent wastewater to that in the treated effluent is shown in Figure 2-3. As shown, the BWTP has been effective, under most circumstances, in reducing the concentration of 2,4-DNT to levels below the discharge limits. Detailed evaluation to determine the removal mechanisms for 2,4-DNT by the BWTP are being initiated by Alliant.
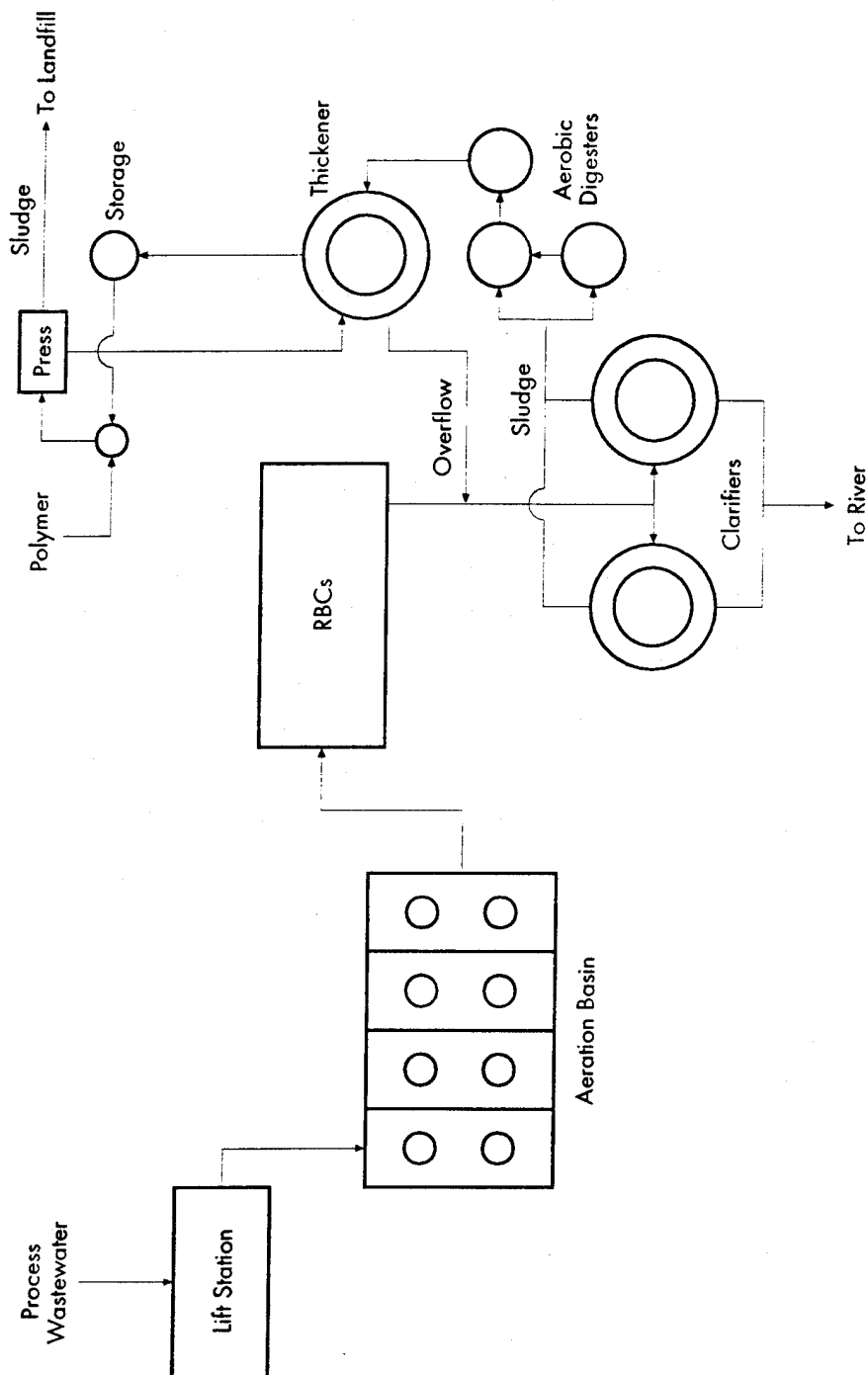
Figure 2-2.
Schematic of RAAP's Biological
Wastewater Treatment Plant (BWTP).

Figure 2-3
Historical Performance of the RAAP BWTP
(Prior to Plant Expansion)
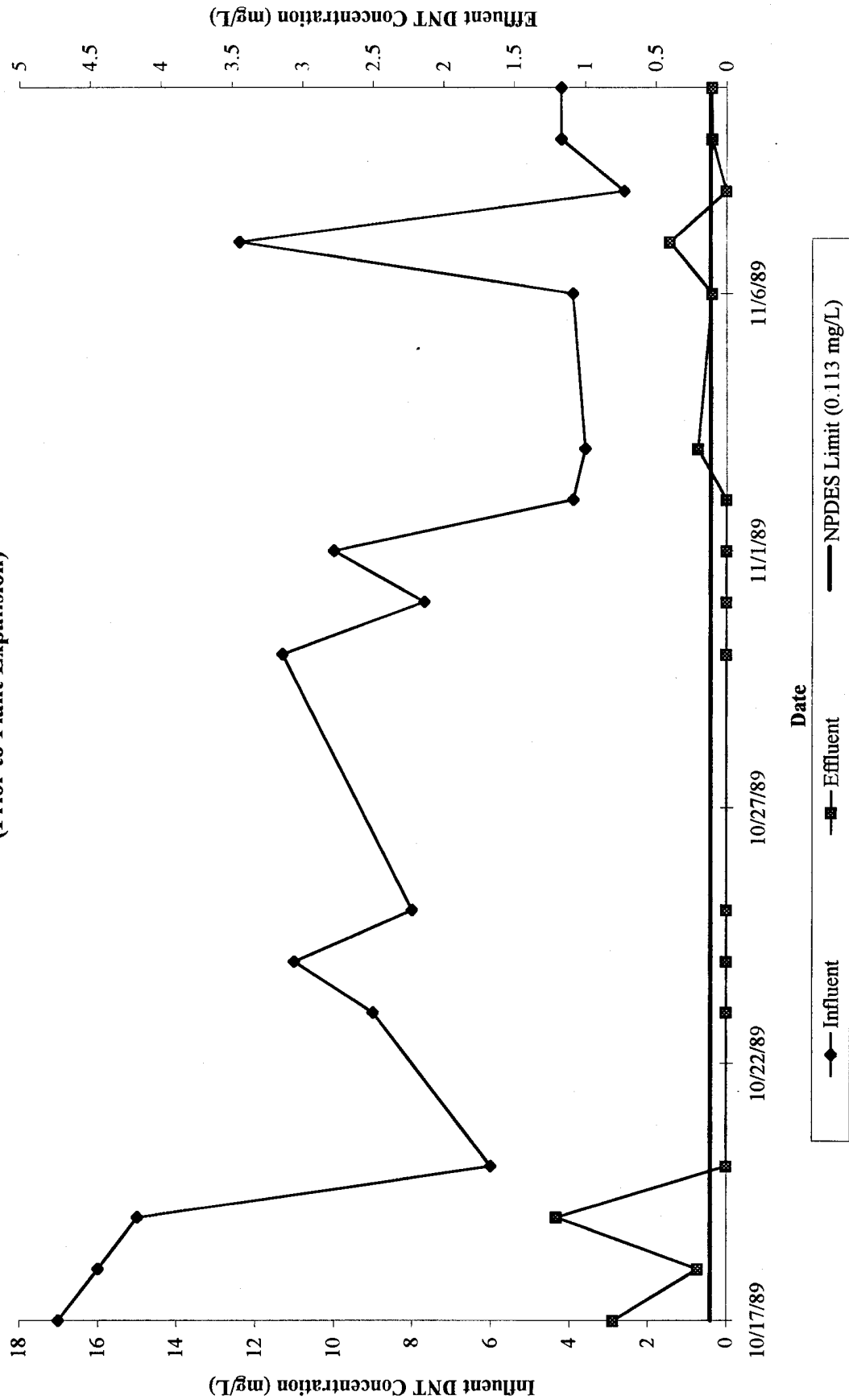
2.3 Demonstration Facilities

The pilot-scale demonstrations were housed in one of the inactive WD Buildings, Building No. 1672. This project location was selected because of its proximity to the source of WD wastewater and the industrial sewer. To facilitate placement of the pilot-scale demonstration treatment systems, two wooden stave WD process tanks were removed from the building prior to the study. An existing closed-top, fiberglass storage tank located in Building No. 1672 was left in place and used as a holding tank for temporary storage of WD wastewater prior to treatment in the pilot-scale test units. The storage tank had a capacity of approximately 20,000 gallons. A schematic diagram of the demonstration building is shown in Figure 2-4.

WD wastewater was intercepted at Manhole No. 32 (MH32) which is located adjacent to Building No. 1672. WD wastewater discharges from WD Buildings Nos. 1665, 1667, 1669, and 1670 flows through the industrial sewer that is accessed by MH32. Collection of WD wastewater was coordinated with Alliant's propellant production staff who scheduled the water-dry operations. As WD tanks were scheduled to be drained, the project team was notified and mobilized to collect available wastewater. Wastewater was pumped from MH32 to the fiberglass storage tank in Building No. 1672 using air driven and gasoline powered pumps, and temporary double-lined hoses. Production schedules dictated the volume of WD wastewater and determined when it was available. Demonstration tests were, therefore, scheduled to coincide with these events. After collection, the wastewater was metered from the storage tank to the demonstration systems. After the wastewater passed through the pilot-scale treatment units, it was returned by gravity flow to the industrial sewer via MH32 at a point downstream from the point of initial interception. The treated effluent from the demonstration systems, therefore, flowed to the BWTP and was treated with all other industrial wastewaters in the usual manner. The WD buildings are equipped with floor drains that flow to the industrial sewer. Therefore, any spills in the building were contained. A review of the planned demonstrations was conducted with the environmental staff at RAAP, based on these discussions and discussions held between Alliant and the State, it was determined that no environmental permits were required for the demonstration.
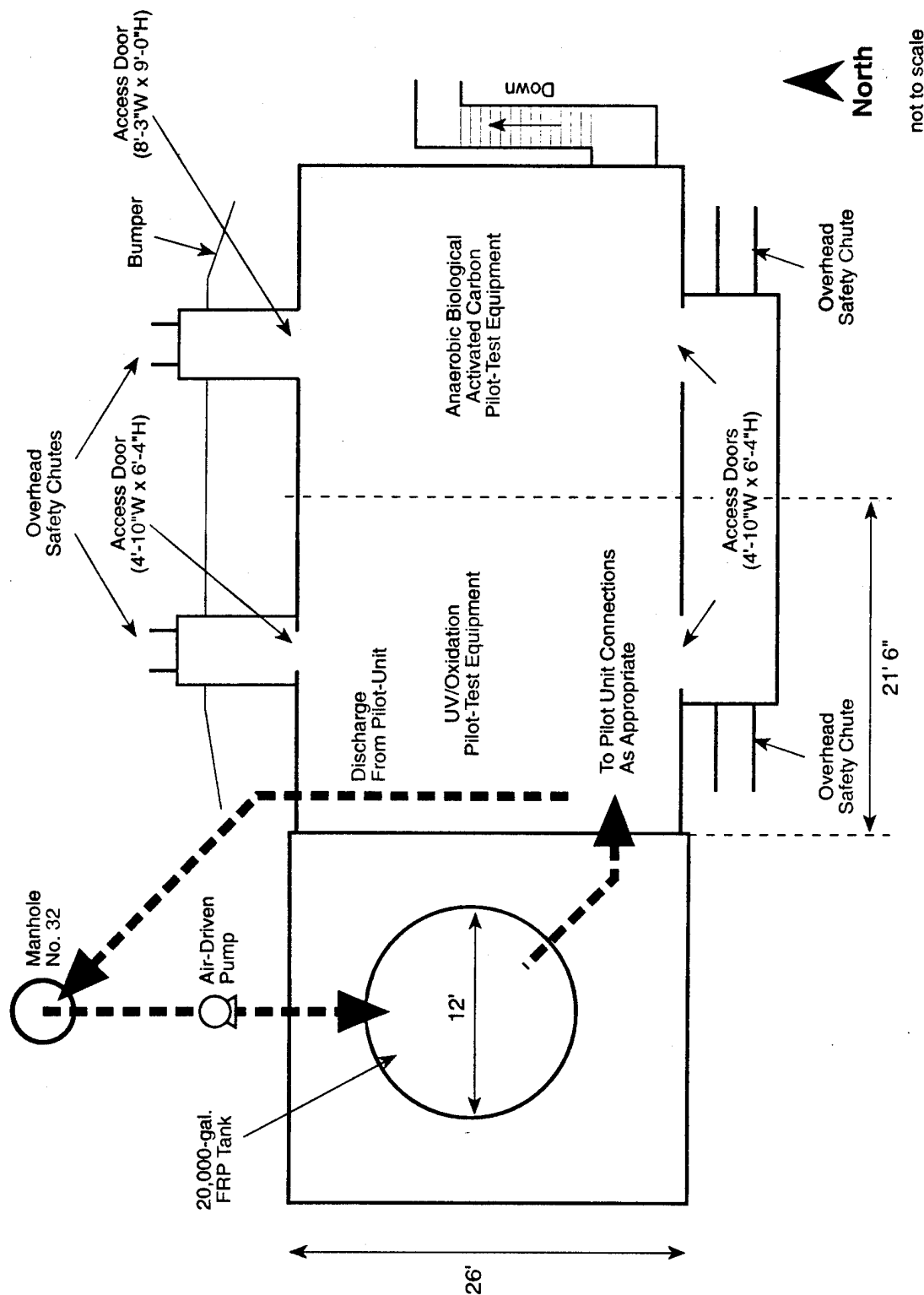
Figure 2-4. Schematic of wastewater treatment test area.

Access Door (8'-3"W x 9'-0"H)

Bumper

Down

North

not to scale

Overhead Safety Chute

Anaerobic Biological Activated Carbon Pilot-Test Equipment

Overhead Safety Chutes

Access Door (4'-10"W x 6'-4"H)

Access Doors (4'-10"W x 6'-4"H)

Discharge From Pilot-Unit

UV/Oxidation Pilot-Test Equipment

To Pilot Unit Connections As Appropriate

Overhead Safety Chute

21' 6"

Manhole No. 32

Air-Driven Pump

20,000-gal. FRP Tank

12'

26'

INTERNATIONAL TECHNOLOGY CORPORATION

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S-322245-5/94-1b

3.0 TECHNOLOGY SELECTION

An initial step in the technology demonstration process was completion of a review of the literature and previous studies conducted by the USAEC, the USACERL, and others regarding treatment of DNT in wastewater. The purpose of this review was to acquire the information necessary for selection of technologies to be evaluated by pilot-scale demonstration. The rationale used for selection of the technologies included in the demonstration at RAAP was documented and accepted by the USAEC.[4] A summary of the findings of this effort is presented in the following paragraphs.

A previous study conducted by the USAEC concluded that interception and treatment of DNT bearing wastewater upstream of the BWTP could potentially alleviate DNT discharge problems.[2] This study provided the basis and impetus for further evalution. It concluded that DNT wastewaters could be intercepted at a location near the source, such as MH32, and recommended further efforts to identify and demonstrate potentially applicable technologies.

Subsequently, the USACERL conducted an investigation regarding the feasiblity of using an anaerobic biological treatment process in a fluidized bed of granular activated carbon.[3] Laboratory and bench-scale studies were performed using both a laboratory prepared solution of DNT and actual WD wastewater generated at RAAP. It was concluded that this technology offered favorable prospects for this application and warranted further study at the pilot-scale.

During the review of the general literature, databases including Water Resources Abstracts, National Technical Information Services, the Engineering Index Compendex and other computerized information systems were accessed to identify candidate technologies. Successful treatment of DNT, or an analogous compound, in wastewater at bench-scale was set as the minimum criterion for consideration of a technology. The search identified six potentially applicable technologies:

- Anaerobic Fluidized-Bed Biological Reactors with Granular Activated Carbon (AnFBR)
- Anaerobic Biological Reactors with Synthetic Resins (AnBSR)
- Granular Activated Carbon (GAC)

- UV/ Oxidation (UV/OX)
- Rotating Biological Contactors (RBC)
- Sequencing Batch Reactors (SBR)

A brief summary of the information obtained regarding these wastewater treatment technologies and the capability to treat DNT or selected refractory compounds is presented below. The selection process resulted in the elimination of AnBSR and SBR technologies while retaining AnFBR, UV/OX, GAC and RBC for further consideration. Evaluation of the retained technologies and the basis for selection of both a UV/OX system and an AnFBR system followed by a RBC is presented in Table 3-1.

Anaerobic Fluidized-Bed/Biological Reactor with Granular Activated Carbon (AnFBR)

Much of the previous work with AnFBR reactors has focused on wastewaters associated with coal gasification, thermoplastic resin manufacture, and wood treating processes. These inhibitory wastewaters can contain phenol or polycyclic N-aromatic compounds. Bench and pilot-scale applications have achieved removals exceeding 99 percent for phenol.[5] Wang, Suidan, and Pfeffer (1984) suggested that continuous treatment of wastewaters containing adsorbable refractory and inhibitory constituents (polycyclic N-aromatic compounds) with a GAC expanded bed filter is possible if a partial GAC replacement schedule is established to maintain the concentration of toxic constituents below a threshold level.[6] Others have shown that periodic GAC replacement is not necessary for treatment of leachates containing volatile and semivolatile compounds such as phenol, nitrobenzene, 1,2,4-trichlorobenzene, and dibutyl phthalate.[7] Narayanan, Suidan, Gerderloos, and Brenner fed a synthetic wastewater containing inhibitory semivolatile organic compounds to an anaerobic expanded bed GAC reactor.[8] Nitrobenzene, p-nitrophenol and lindane were completely removed by biodegradation.

USACERL assessed the use of anaerobic expanded bed GAC reactors specifically for 2,4-DNT removal in wastewater.[3, 9] These studies concluded that anaerobic expanded bed GAC reactors represent a potentially viable technology for treating 2,4-DNT wastewater. The GAC adsorbs the 2,4-DNT that exceeds the assimilative capacity of the bacterial population. The 2,4-DNT stored

Table 3-1

Preliminary Technology Evaluation Matrix for Pre-Treatment of 2,4-DNT in Wastewater

Treatment Technology	Refractory Compounds	DNT Treatment	Pilot Testing Recommendation	Comments
Anaerobic Fluidized-Bed Biological Reactor with Granular Activated Carbon (AnFBR)	Successful	Successful	Recommended	• Proven ability to degrade 2,4-DNT in RAAP Wastewater. • Biodegradation of carbon is advantageous.
Ultra-Violet Oxidation with Ozone/Hydrogen Peroxide	Successful	Successful	Recommended	• Proven ability to degrade 2,4-DNT. • Vendor literature claims to remove 2,4-DNT with ozone based system.
Rotating Biological Contactor (RBC)	Successful	Successful	Recommended	• Proven ability to remove 2,4-DNT in RAAP wastewater. • Application in series with an AnFBR system would simulate pretreatment followed by aerobic treatment. Information from pilot-scale test could potentially be used to improve operation of RAAP BWTP.
Granular Activated Carbon (GAC)	Successful	Successful	Not Recommended	• Proven ability to remove 2,4-DNT in wastewater. • Adequate information available from other sources to allow full-scale design without a pilot-test possible.
Anaerobic Biological Reactor with Synthetic Resin (AnBSR)	Not Tested	Not Tested	Not Recommended	• Not sufficiently different from AnFBR to warrant separate demonstration.
Aerobic Sequencing Batch Reactor (SBR)	Successful	Not Tested	Not Recommended	• No evidence in literature to show success in 2,4-DNT removal. • Technology not sufficiently different from RBC technology to warrant separate demonstration.

on the GAC is then desorbed when influent concentrations decrease, thus maintaining feed of 2,4-DNT to the bacteria. This process also regenerates the carbon. Thus, the GAC acts as a buffer against fluctuating influent concentrations of 2,4-DNT and provides a support surface for bacterial growth. As a result of anaerobic biodegradation, 2,4-DNT was stoichiometrically reduced to diaminotoluene (DAT) under methanogenic conditions when a primary growth substrate (e.g., ethanol) was present.

The bench-scale study conducted by USACERL included testing of laboratory prepared wastewater at various flow rates and concentrations of 2,4-DNT. The results indicated that the system was capable of handling large fluctuations in influent concentrations (40 to >700 mg/L 2,4-DNT) without substantial breakthrough. The system achieved greater than 99.5 percent removal and was capable of reducing levels of 2,4-DNT to below detection. The observed carbon loading (600 mg 2,4-DNT/g carbon) was also higher than previously reported isotherms obtained from batch adsorption studies (200 to 400 mg/g carbon). Little DAT was produced indicating that the DNT underwent full anaerobic biodegradation to methane gas.

Subsequent studies by USACERL were performed at the RAAP using actual wastewater obtained directly from an active WD process. These studies showed the technology is capable of achieving greater than 99 percent removal of DNT and achieving effluent concentrations below the target limit of 113 µg/L. DAT was reported to be the product of DNT degradation. The GAC/anaerobic combination was also reported to be versatile in handling shock loading and upset conditions caused by sudden rise in ether and alcohol concentrations.

Advantages reported in the literature for treatment in AnFBR reactors are:
- AnFBR reactors can withstand variations in the influent concentrations due to the adsorptive capacity of the activated carbon.
- AnFBR reactors are capable of bioregeneration, through adsorption and subsequent desorption, thereby eliminating the expense of replacement or reactivation of spent carbon as is necessary in conventional activated carbon adsorption.
- There is no oxygen requirement and methane gas generated by the anaerobic organisms may have potential for use.
- There is little or no sludge produced from AnFBR reactors as opposed to aerobic activated sludge processes.

Disadvantages of AnFBR systems include:

- The relatively long retention times required for effective treatment may result in a system that is not economical to construct and operate.
- Methane gas generated may require special handling.

Based on the proven ability of this technology at the bench-scale to successfully treat WD wastewater and the advantages offered by the system, AnFBR was recommended for further study at the pilot-scale.

Anaerobic Biological Reactors with Synthetic Resins (AnBSR)

The general literature search revealed limited information regarding the use of synthetic resins in anaerobic biological treatment of wastewater. The review focused on possible advantages of synthetic resins over GAC (such as greater adsorptive capacity or the ability to sustain anaerobic microbial populations). Synthetic resins have been used in continuous polymeric adsorption processes to remove TNT and DNT from waste streams at the Iowa Ammunition Plant. The non-ionic polymeric sorbent Amberlite XAD-4 was shown to reduce TNT levels from 70-120 mg/L to below 1 mg/L from the ammunition plant waste stream.[10] DNT was known to be present in the wastewater, however, results for DNT removals were not reported.

Synthetic resins have been selected to replace conventional GAC in adsorption treatment processes for removing explosives from waste streams because of the difficulties encountered when regenerating carbon contaminated with explosives (i.e. limited success with thermal regeneration).[11] Synthetic resins can be regenerated with solvent or, in some cases aqueous solutions, and will retain a high percentage (greater than 90 percent) of their original capacity.[12] The solvent can be recovered for reuse, leaving a concentrated aqueous sludge of explosive contaminant for disposal.[10]

Synthetic resins and activated carbon have been compared as support material for methanogenic phenol degrading anaerobes. Both XE-352 anion-exchange resin and activated carbon exhibited favorable qualities as support for development of biomass. The XE-352 resin exhibited superior qualities (more accessible surface area) than the activated carbon for rapid microbial growth, but

the anion-exchange resin did not absorb phenol. Therefore, this resin could not be utilized to remove inhibitory compounds, such as DNT, from waste streams.

AnBSR was not considered to be sufficiently different from AnFBR to warrant a separate pilot-scale test. AnBSR may represent a potential improvement of the AnFBR technology which itself has yet to be proven in this application on a pilot-scale basis. Further, sufficient bench-scale and laboratory tests have not been performed to support the proper selection of a synthetic resin for a pilot-scale system. Therefore, AnBSR was not recommended for pilot-scale demonstration.

Granular Activated Carbon (GAC)

GAC has long been known to be effective in removing 2,4-DNT from wastewater. Laboratory tests to obtain adsorption isotherms for carbon adsorption of 2,4-DNT have been conducted at RAAP.[2] The isotherm studies indicated that 2,4-DNT was easily adsorbed on carbon; however, the carbon's adsorptive capacity decreased substantially in the presence of competing solvents such as alcohols or ethers. Bench-scale tests indicated that more 2,4-DNT was being adsorbed than predicted from the isotherm and confirmed that the adsorptive capacity was reduced with the addition of solvent in the influent.

GAC is proven technology that has been extensively used to treat a wide variety of contaminants in conventional wastewater treatment systems. The design of GAC systems is well established and a pilot-scale demonstration is not necessary for implementation. Therefore, although GAC is recommended as a technology for further consideration, a demonstration was not recommended for this technology.

UV/OX

Advanced oxidation processes, such as ultraviolet radiation in combination with either ozone, hydrogen peroxide, or both, are effective as pretreatment or polishing steps.[13] A recent USEPA report suggests that the technology can be applied to industrial wastewater contaminated with semi-volatile compounds.[14] Removal efficiencies for volatiles in groundwater treated with ultraviolet radiation and ozone were reported to vary from 40 to 99.99 percent; removals for semi-volatile compounds were not addressed. Others have shown that UV radiation and

hydrogen peroxide will degrade 2,4-DNT in aqueous solution.[15] UV/OX equipment vendors also presented claims of proven ability to treat DNT.

Laboratory evaluations of UV/OX previously conducted by USAEC indicated that UV/Ozone appeared to be a more effective combination than UV/Peroxide.[2] Subsequent bench-scale tests of this technology were limited to UV/Ozone. These tests indicated that 2,4-DNT could be destroyed effectively, with few by-products. The rate of DNT destruction was found to be directly proportional to the quantity of UV radiation, and independent of ozone flow rate beyond a threshold ozone level.

Advantages associated with UV/OX treatment are that:
- treatment has been shown to be effective in removal of 2,4-DNT from wastewaters
- the technology can be used to treat a stream characterized by intermittent flows
- modular skid mounted systems are available.

Some disadvantages are:
- high energy consumption
- treatment is limited by mass transfer of ozone in the liquid,
- wastewater must be free of significant scavengers (i.e., species that consume oxidants) as well as suspended solids, and oil and grease that can build-up on the quartz tubes used to cover the UV lamps, and
- the potential exists for toxic effluent from hydrogen peroxide residual when combining UV and hydrogen peroxide.

Based on the successful bench-scale study performed by USAEC and on vendor claims of prior successful treatment of 2,4-DNT, UV/OX was recommended for pilot-scale evaluation.

Rotating Biological Contactors (RBC)

USAEC previously performed laboratory and bench-scale tests to evaluate biodegradation of DNT on RBCs.[2] Laboratory studies indicated that DNT was not toxic to acclimated biomass and did not bioaccumulate significantly. The biomass was successful in degrading DNT, however, biotransformation products were not identified. Bench-scale tests were conducted, using an RBC with 9-inch diameter disks, also showed that 2,4-DNT may be reduced by biological degradation.

RBCs are currently used in the BWTP as the technology to treat industrial wastewaters generated at RAAP. Bench-scale tests have shown that 2,4-DNT at higher concentrations than normally present at the RAAP BWTP is not toxic to RBCs. It was recommended that RBC technology be included in the pilot-scale demonstration to treat the effluent from the AnFBR system in order to obtain information on the fate of DNT and DAT. Furthermore, the pilot-scale results could produce useful information for future improvements to the operation of the existing BWTP.

Sequencing Batch Reactors (SBR)

Bench-scale soil slurry sequencing batch reactors have been used to treat explosives contaminated soils and sequencing batch biofilm reactors have been used to treat explosives contaminated groundwater at the Newport Army Ammunitions Plant.[16] DNT was present in the soil and the groundwater, however only TNT removals were reported. Information regarding the use of SBRs for treatment of DNT in wastewater was not found in the literature. This technology was not considered to be sufficiently different from RBCs to warrant separate pilot-scale investigation. Furthermore, sufficient data for treatment of DNT in SBRs is not available from literature sources to permit design of a pilot-scale SBR. Therefore, this technology was not recommended for further evaluation.

Budgetary cost estimates were prepared for the four systems considered suitable for pilot-scale demonstration. The cost estimates indicated that the present worth costs for each of the four systems evaluated are of the same order of magnitude and comparable. Therefore, an economic basis for rejection of any of the technologies from further consideration was not apparent. Based on the analysis of the available information, the following technologies were recommended for pilot-scale demonstration at RAAP:

- Anaerobic Biological Granular Activated Carbon Reactors (AnFBR) followed by rotating biological contactors (RBC)
- UV/ Oxidation (UV/OX)

4.0   DEMONSTRATION OF UV/OX

The equipment and methodology used, and the results of the pilot-scale demonstration of UV/OX treatment of WD wastewater at the RAAP are summarized in this section.

4.1 UV/OX Theory

Advanced oxidation processes (AOPs), such as ultraviolet radiation in combination with either ozone, hydrogen peroxide, or both, can be effective as wastewater pretreatment or polishing steps. AOPs have been described as oxidation processes that are based on the generation of hydroxyl radical intermediates.[17] UV/OX uses ultraviolet radiation in combination with oxidants, such as ozone (O_3), hydrogen peroxide (H_2O_2), or both, to produce hydroxyl radicals. Table 4-1 presents the oxidation potential of different oxidizing radical species. Hydroxyl radicals are second only to fluorine in their oxidation potential and have been shown to be effective in the treatment of industrial wastewaters.[13]

Table 4-1. Oxidation Potential of Different Chemical Species

Species	Oxidation Potential (volts)
Fluorine (F_2)	3.06
Hydroxyl Radical (OH^-)	2.80
Atomic Oxygen (O)	2.42
Ozone (O_3)	2.07
Hydrogen Peroxide (H_2O_2)	1.77
Perhydroxyl radicals, ($O.OH^-$)	1.70
Hypochlorous Acid (HOCl)	1.49
Chlorine (Cl_2)	1.36

Source Reference 18

The following reaction pathway for photo-oxidation by UV/H_2O_2 of aqueous 2,4-DNT solutions has been suggested:[15]

> 2,4-DNT --> 2,4-dinitrobenzyl alcohol --> 2,4-dinitrobenzaldehyde --> 2,4-dinitrobenzoic acid --> 1,3-dinitrobenzene --> 3-nitrophenol + dinitrophenols ($+NO_3^-$) --> dihydroxynitrobenzenes --> trihydroxynitrobenzenes --> nitromuconic acid derivatives ($+NO_3^-$) --> maleic acid + nitro- and hydroxymaleic acid derivatives + glyoxal + glyoxylic acid --> oxalic acid + formic acid ($+ NO_3^-$) --> $CO_2 + H_2O$
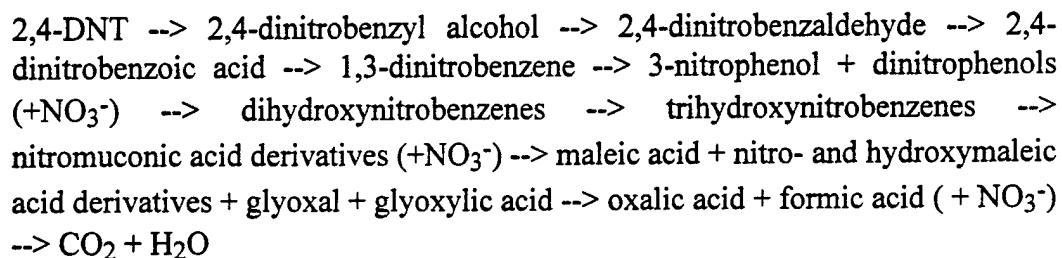
As shown, complete mineralization of 2,4-DNT to carbon dioxide and water is theoretically possible. However, examination of the reaction intermediates shown above indicate that several of the intermediate species are also biodegradable. Transformation of 2,4-DNT to a biodegradable intermediate could therefore increase the effectiveness of treatment of the wastewater by the existing aerobic BWTP if complete mineralization is not achieved.

4.2 Selection of Equipment

The previous bench-scale study conducted by the USAEC to investigate the treatment of 2,4-DNT showed that use of ozone and UV light at a frequency of 254 nm was capable of destroying 2,4-DNT in wastewater.[2] Several degradation by-products were noted in the effluent during the previous study. These by-products appeared to be destroyed by prolonged exposure to UV and ozone. The use of a catalyst was shown not to be required for the technology to be successful.

Based on the available information, technical specifications were prepared to solicit bids from UV/OX equipment vendors. The technical specifications required a system capable of operating at flow rates of 1 to 5 gpm, use 254 nm UV lights, and supply ozone and hydrogen peroxide as oxidants, either alone or in combination. Five vendors responded to the request for bids. Based on a technical and economic evaluation, an Ultrox Model P-650 was selected for the demonstration.

4.3 Equipment Description

The Ultrox Model P-650 consisted of four main units:

- a UV reactor.

- an ozone generator and accompanying air compressor, filter, and dryer.
- a hydrogen peroxide feed tank and pump.
- an ozone decomposer (the Decompozon®).

A schematic of the UV/OX system used for the demonstration is shown in Figure 4-1. Figure 4-2 shows the process flow diagram for the system. The UV/OX reactor had a total volume of 650 gallons and was partitioned by weirs into six cells of equal volume. Wastewater entered the reactor at the bottom of Cell 1 and exited at the bottom of Cell 6. Each cell contained 12 low-pressure UV lamps (with a wavelength of 254 nm) totaling 780 watts (W), for a maximum of 4.68 kW of UV light intensity in the reactor. All, one-half, or none of the UV lamps in each cell could be turned on to provide various intensities of UV radiation. Samples could be taken from any cell to assess treatment at different wastewater retention times. The wastewater influent flowrate could be varied from 0 to 60 gpm while the ozone flowrate could be varied from 2.8 to 28 pounds/day. The hydrogen peroxide flowrate could also be varied. The ozone generator required 7 gpm of cooling water.

The oxidants used during demonstration were ozone and hydrogen peroxide, both individually and in combination. Hydrogen peroxide was metered into the system at the wastewater inlet using a diaphragm pump. Ozone was bubbled into each of the six reactor cells in equal amounts. Thus, whereas the entire hydrogen peroxide dose was injected into the wastewater at one point (i.e., the inlet), the total ozone dose was distributed equally across the six reactor cells. The offgas, including any unreacted ozone, was treated in the ozone decompozer for destruction of ozone prior to discharge to the atmosphere.

During the demonstration, analytical samples were withdrawn from the following locations (shown on Figure 4-2):

SP2   Wastewater influent to the UV/OX system
SP4   Cell 2 Sample
SP6   Cell 4 Sample
SP7   Cell 5 Sample (Run No. 5 only, as discussed later)
SP9   Effluent Sample

The sample ports were located at the mid-point of the cells.

Figure 4-1. Process flow diagram – Ultrox Pilot-Scale UV/OX Test System.

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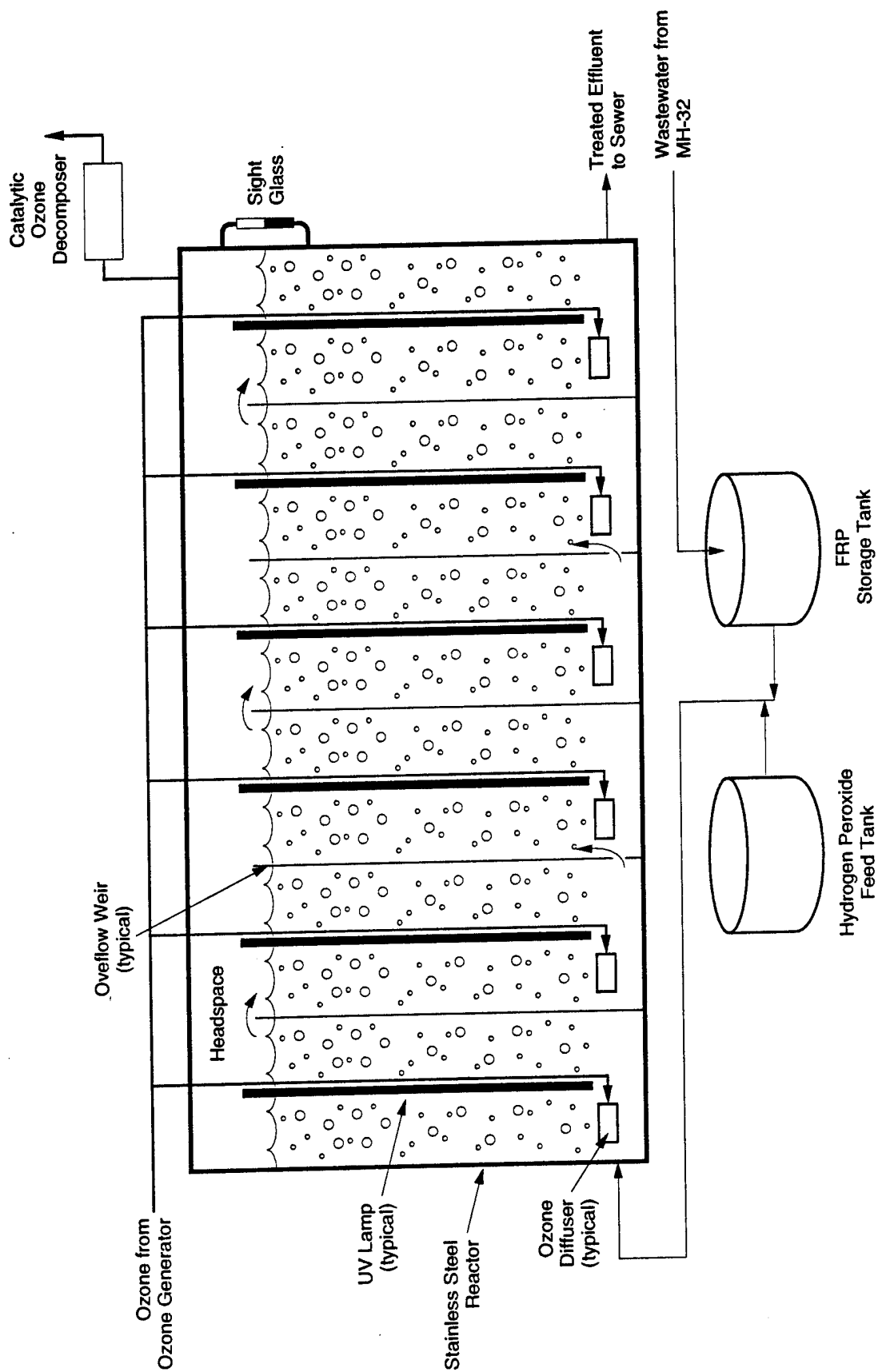
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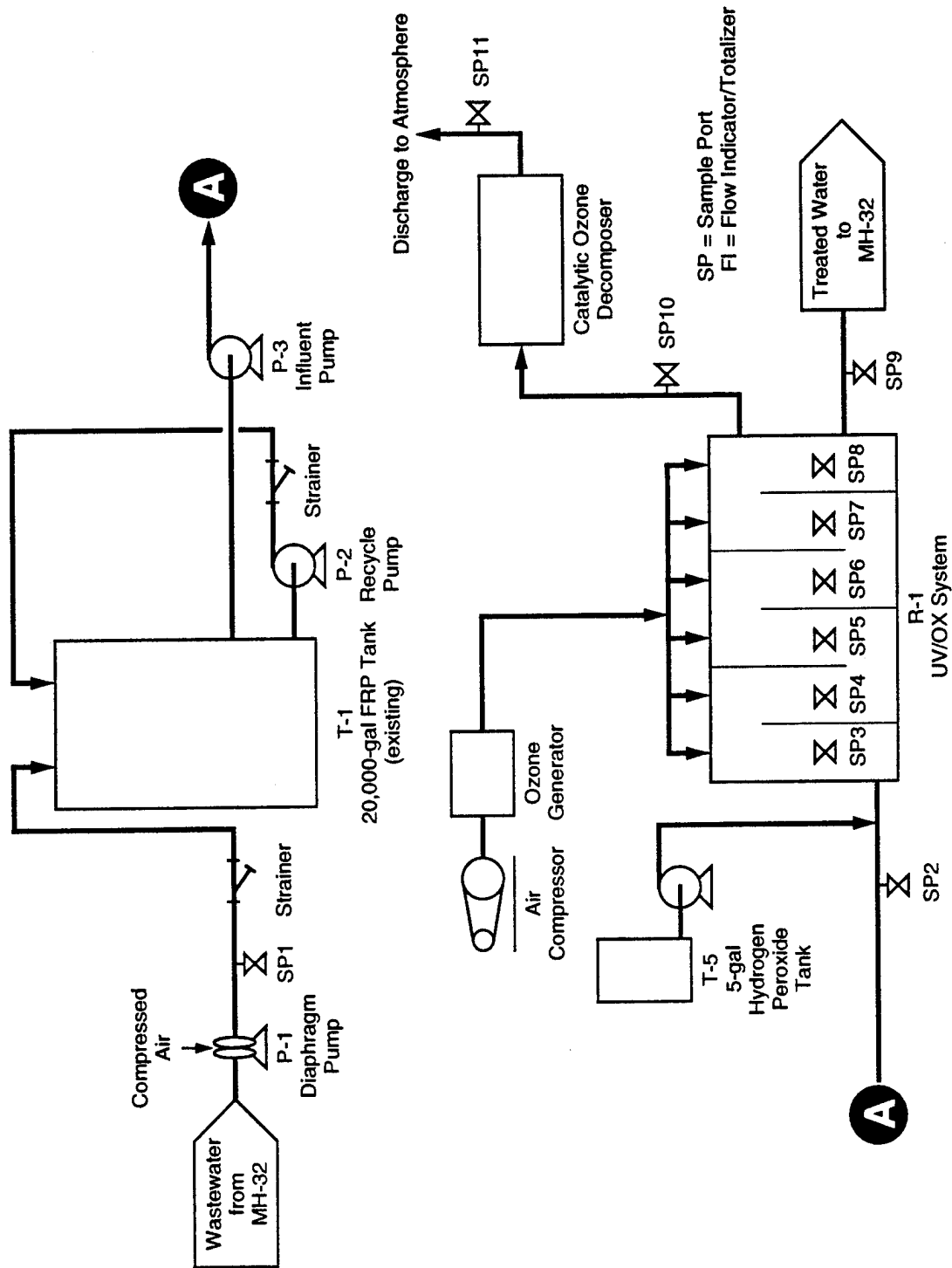
Figure 4-2. Process flow diagram – UV/OX Test System.

SP = Sample Port
FI = Flow Indicator/Totalizer

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Prior to each test or change of conditions, the system was operated for a period equal to at least three residence times to allow steady-state conditions to be reached prior to the initiation of sampling. Three samples were taken, at 30 minute intervals, from the sample ports identified above during each run. During one of the runs (Run No. 5), a sample was also taken from Cell 5 (SP7) to acquire additional data for tracking 2,4-DNT destruction across the reactor.

4.4 Demonstration Methodology

A total of nine test runs were performed with the UV/OX system. Four operating parameters were varied to evaluate performance of the UV/OX system in terms of 2,4-DNT removal efficiency: retention time, ozone dosage, hydrogen peroxide dosage, and UV radiation intensity. Table 4-2 presents the matrix of operational conditions that was used to evaluate these parameters during the demonstration and provides the test conditions used for each run. Development of this test matrix was based on the review of the literature and on information supplied by the equipment vendor. The ozone and hydrogen peroxide dose rates used for Run Nos. 1, 2, and 3 were selected based on the available literature and vendor recommendations. Subsequent dose rates and retention times (for Run Nos. 4 and 5) were determined based on the results of the initial three runs. Conditions for Run Nos. 6, 7, and 8 were then determined after the first five runs were examined and additional data needs were determined. During Run No. 9, the test unit was operated in a batch mode allowing extended retention times to be achieved to determine the maximum destruction of 2,4-DNT.

The 20,000-gallon fiberglass storage tank was filled once with available WD wastewater prior to commencing the test runs. The first four test runs were conducted using a single batch of WD water collected in the 20,000-gallon tank. At the conclusion of these test runs, the water in the tank was exhausted and a new batch was collected from MH 32 during the next generation of WD effluents. WD wastewater was not available continuously because production schedules at RAAP dictated the availability and generation schedule of WD wastewater. The demonstration was conducted during a brief production campaign and used all available WD effluent.

Table 4-2. Operating Conditions Used During the UV/OX Test Runs.

Test Run No.	Wastewater Flowrate (gpm)	Hydrogen Peroxide Flowrate (ml/min)	Ozone Flowrate (cfh)	Total Oxidant Dosage (mg/l)	UV (Percent of Lamps On)
1	5	21	0	440	100
2	5	0	500	420	100
3	5	5	380	420	100
4	2.5	5	380	840	100
5	1.5	7	500	1,900	100
6	2.5	2.5	190	420	100
7	2.5	5	380	840	50
8	1.5	5	380	1,400	100
9	Batch	5	380	2,300	100

Retention Time

The effectiveness of UV/OX systems in treating organics is a function of retention time. The longer the wastewater remains within the treatment system, the greater the propensity for UV light to penetrate the solution, stimulating formation of hydroxyl radicals from the oxidants and cleaving existing organic molecular bonds. A threshold is reached at which point increasing retention times do not significantly increase contaminant destruction rates. It was the intent of the testing program to evaluate the effects of hydraulic retention time on the mineralization of 2,4-DNT.

Information supplied by the equipment vendor, based on their prior experience with similar waste streams and confirmed by data from the USACERL research, suggested that destruction of DNT in wastewater would require from 40 to 120 minutes of retention time.[8,19] The previous USACERL study also found that destruction of 2,4-DNT was inhibited by the presence of solvents such as alcohol and ether. Mineralization of these solvents provided competition for the hydroxyl radical reducing the amount available to treat 2,4-DNT. It was anticipated that the time required to destroy 2,4-DNT in the WD wastewater would be greater because the WD wastewater contains significant quantities of both ethanol and ether. As mentioned above, the demonstration system had sample ports located in the center of each of its six sequential reactor cells. As the wastewater flows through each cell, it experiences a longer retention time. The retention times are calculated to the mid-point of each cell. Thus, for example, to calculate the retention time for Cell No. 2, the total reactor volume is divided by the wastewater flow rate and multiplied by 1.5. For Cell No. 4, this multiplier is 3.5, whereas for the effluent the multiplier is 6. At a flowrate of 5 gpm, retention times of 33 minutes in Cell No. 2, 76 minutes in Cell No. 4, and 130 minutes in the reactor effluent (after Cell No. 6) could be evaluated during a single run. Flowrates other than 5 gpm were also used to achieve different retention times based on the results of the initial runs.

Oxidant Dosage

Oxidants (ozone and/or hydrogen peroxide) provide the source of hydroxyl radical necessary for efficient destruction of organic compounds. Generally, increasing oxidant dosage provides more hydroxyl radicals for greater destruction of organics and increases the mineralization capabilities

of the UV/OX system. Laboratory evaluations of UV/OX performed during an earlier study indicated that the rate of 2,4-DNT destruction was independent of oxidant dosage once a threshold oxidant level was achieved.[2] Various dosing levels of ozone and hydrogen peroxide were evaluated to determine if either one, or a combination of both, would result in more efficient treatment.

Oxidant dosages, for both ozone and hydrogen peroxide, are typically measured in mg/l (milligrams of oxidant per liter of wastewater). The dosage is a function of the oxidant flowrate and the retention time of the wastewater -- a longer retention time allows more oxidant to contact the wastewater in the reactor. Based on available data, 425 mg/l of total oxidant was selected as the initial dosage used during the demonstration.

As mentioned previously, the Ultrox test unit used different delivery modes for ozone and hydrogen peroxide. The total hydrogen peroxide dosage is injected at only one point, the reactor influent, while the total ozone dosage is divided into six equal amounts and injected into each of the six reactor cells. Thus, each successive reactor cell experiences an increasing cumulative ozone dosage, whereas, for hydrogen peroxide, each cell experiences the same dosage. However, the total oxidant dosage experienced by the effluent is the same whether ozone or hydrogen peroxide or both are used. The oxidant dosage that each reactor cell experienced for each run is shown in Table 4-3. The ability to sample each reactor cell allowed the demonstration to be completed with fewer total test runs because multiple retention times and oxidant dosages could be evaluated during a single run.

UV Light Intensity

UV light provides an energy stimulus for formation of hydroxyl ions. UV light also provides sufficient energy to cleave some organic molecular bonds. Increasing the quantity of UV radiation (i.e., by increasing the number of lamps in operation) has been shown in laboratory tests to increase the rate of mineralization of 2,4-DNT. However, as with retention time and oxidant dosage, a point of diminishing returns is reached where energy consumption increases without a corresponding increase in destruction efficiency.

Table 4-3
Oxidant Dosages in Each Reactor Cell During the UV/Oxidation Test Runs

Run No.	Cell No.	Wastewater Flow Rate (gpm)	Retention Time* (min)	Ozone Flow Rate (cfh)	Ozone Flow Rate (lbs/day)	Ozone Concentration▼ (mg/l)	35% Hydrogen Peroxide Flow Rate (ml/min)	35% Hydrogen Peroxide Flow Rate (lbs/day)	35% Hydrogen Peroxide Concentration (mg/l)	Total Oxidant Dosage Concentration (mg/L)	Total Oxidant Dosage Concentration (mmol/L)	H₂O₂:O₃ Ratio
1	2	5	32.5	0	0	0	21	26	110	110	3.2	N/A
	4		75.83	0	0	0	21	26	256	256	7.5	N/A
	Effluent		130	0	0	0	21	26	439	439	12.9	N/A
2	2	5	32.5	500	25	104	0	0	0	104	2.2	0.00
	4		75.83	500	25	242	0	0	0	242	5.0	0.00
	Effluent		130	500	25	415	0	0	0	415	8.6	0.00
3	2	5	32.5	380	19	79	5	6	26	105	2.4	0.33
	4		75.83	380	19	184	5	6	61	245	5.6	0.33
	Effleunt		130	380	19	315	5	6	105	420	9.6	0.33
4	2	2.5	65	380	19	158	5	6	52	210	4.8	0.33
	4		151.67	380	19	368	5	6	122	490	11.2	0.33
	Effluent		260	380	19	630	5	6	209	839	19.3	0.33
5	2	1.5	108.33	500	25	346	7	9	122	467	10.8	0.35
	4		252.78	500	25	806	7	9	285	1,091	25.2	0.35
	5		325	500	25	1037	7	9	366	1,402	32.4	0.35
	Effluent		433.33	500	25	1382	7	9	488	1,870	43.1	0.35
6	2	2.5	65	190	9	79	2.5	3	26	105	2.4	0.33
	4		151.67	190	9	184	2.5	3	61	245	5.6	0.33
	Effluent		260	190	9	315	2.5	3	105	420	9.6	0.33
7	2	2.5	65	380	19	158	5	6	52	210	4.8	0.33
	4		151.67	380	19	368	5	6	122	490	11.2	0.33
	Effluent		260	380	19	630	5	6	209	839	19.3	0.33
8	2	1.5	108.33	380	19	263	5	6	87	350	8.0	0.33
	4		252.78	380	19	613	5	6	203	816	18.7	0.33
	Effluent		433.33	380	19	1050	5	6	349	1,399	32.1	0.33
9	Effluent	5	120	380	19	291	5	6	97	387	8.9	0.33
	Effluent		240	380	19	582	5	6	193	775	17.8	0.33
	Effluent		360	380	19	873	5	6	290	1,162	26.7	0.33
	Effluent		480	380	19	1,163	5	6	386	1,550	35.6	0.33
	Effluent		600	380	19	1,454	5	6	483	1,937	44.5	0.33
	Effluent		720	380	19	1,745	5	6	579	2,324	53.4	0.33

* - Based on total reactor volume of 650 gallons. Retention times shown are those at the sample ports which were located at the mid-point of each cell.

▼ - Based on ozone/air mixture molecular weight = 26.24

- Total air flow rate containing 2% by weight ozone

The Ultrox unit employed low pressure UV lamps that generate light at a wavelength of 254 nm. The system was initially operated at the maximum UV light intensity of the system (i.e. all the lamps on). Additional testing (i.e. Run No. 7) involved reducing the UV light intensity by 50 percent (i.e. half the lights in each cell were turned off).

The retention time, oxidant dosage, and UV light intensity selected for the first three test runs shown in Table 4-2 were based on best engineering judgment, vendor recommendations, and the anticipated composition of the WD wastewater.

The following operational parameters were monitored to assess and evaluate performance of the UV/OX system during the demonstration runs:

- Flow Rate
- Oxidant Dosage
- 2,4-DNT
- pH
- Temperature
- Hardness (as CaCO3)
- Iron and Manganese
- Alkalinity (as $CaCO_3$)
- Total Suspended Solids (TSS)
- Turbidity
- Chemical Oxygen Demand (COD)
- Alcohol
- Ether

These parameters were selected to allow characterization of the waste stream, assess the effectiveness of the UV/OX process, and provide information about potential effects of other wastewater contaminants on the mineralization of 2,4-DNT.

The analyses of 2,4-DNT and other parameters shown above were performed on-site by the Alliant Technical Analytical Group. The analytical results were available within 24 hours of the time a sample was submitted to the laboratory. This rapid turnaround permitted evaluation of data from test runs prior to initiation of the next test run, and, therefore, modification of operational conditions (i.e., retention time, oxidant dosage, and UV light intensity) were made on successive test runs based on knowledge of the results of preceding test runs. The specific operating parameters for Run Nos. 4, 5, and 6 were determined based on the results of Run Nos.

1, 2, and 3 and were set to achieve optimal destruction of DNT and to assess the impacts of various operational conditions.

4.5 UV/OX Demonstration Results

The analytical results from the nine test runs which were conducted are presented in Table 4-4. (The tables and figures referenced in Section 4.5 appear at the end of this section.) Various kinetic rate expressions were evaluated to express the rate of 2,4-DNT destruction achieved by the UV/OX system (Table 4-5). Data obtained from the test runs were tested against these rate expressions to determine if a match could be made with any of the expressions. The analytical results and the reaction rates are summarized in Table 4-6.

Test Run Nos. 1, 2, and 3

Figure 4-3 presents a graph of 2,4-DNT concentrations vs. time for Run Nos. 1, 2, and 3. Each plot is a straight line, suggesting a zero-order reaction. The results of these runs show that the greatest destruction of 2,4-DNT was achieved when ozone and hydrogen peroxide were used in combination. The maximum destruction of 2,4-DNT achieved during these three runs, however, was only 67 percent, and the lowest concentration of 2,4-DNT achieved in the effluent was 36 mg/L. These results indicated that a longer residence time and a higher oxidant dosage were necessary to achieve greater destruction of 2,4-DNT and to approach an effluent concentration near the detection limit for 2,4-DNT (100 µg/L). Therefore, Run No. 4 was designed on the basis of this information to provide twice the residence time and oxidant dosage as Run No. 3.

Test Run No. 4

Figure 4-4 presents a graph of 2,4-DNT concentrations vs. time for Run No. 4. The plot is linear for 2,4-DNT concentrations greater than 24 mg/L, at which point the slope of the graph changes significantly, indicating a shifting-order reaction. Approximately 97 percent of the influent 2,4-DNT was destroyed during this run. However, a significant concentration of 2,4-DNT remained in the effluent. Based on this new rate of reaction equation, it was concluded that, further increases in residence time and oxidant dosage were required to further reduce the concentration of 2,4-DNT in the effluent. The goal of the study was to reduce 2,4-DNT concentrations in the effluent to the detection limit.

Test Run No. 5

The completion of Run Nos. 1 through 4 consumed all available WD wastewater that had been collected and stored. A new batch of WD wastewater was collected for Run No. 5. The wastewater treated during Run No. 5 contained significantly more alcohol than that used for the previous runs -- almost ten times more alcohol than the wastewater used during Run Nos. 1 through 4 (960 mg/L vs. 98 mg/L, on average). During Run No. 5 the flow rate was reduced from 2.5 to 1.5 gpm. Thus the residence time was increased, and the oxidant dosage was doubled as compared to Run No. 4. Figure 4-5 shows a graph of 2,4-DNT concentration vs. time for Run No. 5. This plot shows a significantly slower rate of 2,4-DNT destruction than that observed during Run No. 4. Because the UV/OX reaction is not selective in destruction of organics, the increase in alcohol concentration had the effect of lowering the rate of 2,4-DNT destruction. Oxidant was consumed as it reacted with the increased concentration of alcohol in addition to the 2,4-DNT. The plot for Run No. 5 indicated a zero-order reaction for 2,4-DNT destruction.

Test Run No. 6

Prior to Run No. 6, additional WD wastewater was collected and placed in the storage tank. As a result of the composition of this addition, concentrations of DNT, alcohol, and ether were diluted from the amounts seen during Run No. 5.

Although Run No. 4 was performed at twice the residence time and oxidant dosage as Run No. 3, the initial rate of 2,4-DNT destruction was not appreciably different between the two runs. Thus, the effect of the higher oxidant dosage had to be isolated from the effect of the longer residence time to evaluate if the additional oxidant, and not just the longer residence time, contributed to higher 2,4-DNT destruction. The cost implications of oxidant dosage for a full-scale system are significant. Therefore, to evaluate the effect of lower oxidant dosage rates on 2,4-DNT destruction, Run No. 6 was designed with the same residence time as Run No. 4 but with one-half the oxidant dosage. Figure 4-6 shows a graph of 2,4-DNT concentration versus time for Run No. 6. This plot indicates a shifting-order reaction. The destruction of 2,4-DNT was less than

observed in Run No. 4 (67 percent vs. 97 percent), indicating that higher oxidant dosages are required to achieve higher 2,4-DNT destruction.

Test Run No. 7

Run No. 7 was performed under conditions similar to Run No. 4 with the exception that only one-half of the UV lamps were utilized (6 lamps in each cell vs. 12 lamps in previous runs). This allowed the evaluation of the effect of UV light intensity on 2,4-DNT destruction. Figure 4-7 shows a graph of 2,4-DNT concentration versus time for Run No. 7. In comparison to Run No. 4, Run No. 7 resulted in less destruction of 2,4-DNT, confirming decreased destruction with decreased UV intensity.

Test Run No. 8

The test conditions for Run No. 8 combined those parameters from the previous runs that were shown to be necessary to achieve maximum destruction of 2,4-DNT. Figure 4-8 shows a graph of 2,4-DNT concentration versus time for Run No. 8. The plot indicates a shifting-order reaction and destruction of 97 percent of the 2,4-DNT present. The concentration of 2,4-DNT in the effluent was 1.6 mg/L, however, which was significantly higher than the target effluent concentration of 100 µg/L.

Test Run No. 9

Run No. 9 was conducted to evaluate the maximum potential of the reactor to destroy 2,4-DNT. The reactor was operated in a closed-loop mode (effluent redirected to influent) to provide a batch mode of operation with constantly increasing retention time. Figure 4-9 shows a graph of 2,4-DNT concentration versus time for Run No. 9. Comparing the results of Run No. 9 to Run No. 8, a slightly more rapid rate of 2,4-DNT destruction was achieved during Run No. 9. This can be attributed to the increased efficiency of batch reactors. Run 9 achieved a level of treatment that reduced 2,4-DNT in the effluent levels below detection.

A decrease in pH (see Table 4-6) was observed during each test run. This decrease was expected since acids are formed as by-products of 2,4-DNT destruction.[15] Application of a full-scale system would require evaluation of the need for pH adjustment.

The COD levels in the wastewater were not observed to decrease during the course of the pilot-scale tests corresponding to the decreasing levels of 2,4-DNT, alcohol, and ether in the reactor. This can be attributed to the formation of by-products of 2,4-DNT destruction. Limited attempts to identify potential by-products tentatively indicated that the most likely compounds formed from destruction of 2,4-DNT were 2,4-dinitrobenzaldehyde and 2,4-dinitrobenzoic acid.

The hardness level of the wastewater averaged 70 mg/L. This is considered soft water and long term treatment of the wastewater would not be anticipated to cause hard water scaling on the quartz sleeves of the UV lamps to a degree that would significantly reduce light intensity. The hardness did not change across the reactor vessel.

The alkalinity of the wastewater averaged 60 mg/L at the influent and was non-detect at the effluent. This indicates that alkalinity was neutralized by the acids formed as a by-product of the reaction.

Iron and manganese levels were low in the influent wastewater with a maximum concentration of 3 mg/L. This level is not expected to cause long term treatment problems due to coating or precipitation. The iron and manganese levels remained approximately the same across the reactor indicating that oxidized metals were not settling in the reactor vessel.

Total suspended solids (TSS) and turbidity were also measured across the reactor. TSS levels were low and ranged from 5-20 mg/L. The maximum turbidity level was approximately 10 NTUs. Neither the TSS nor the turbidity varied across the reactor and the levels seen during the demonstration are not expected to interface with the efficiency of UV/OX treatment.

4.6 Evaluation of UV/OX

The efficiency of UV/OX treatment of 2,4-DNT in WD wastewater was found to be largely dependent on the concentrations of ethanol and ether present in the wastewater. During the demonstration, this system was unable to reduce 2,4-DNT concentrations to the target limit except at very high oxidant dosages and extended residence times. The target effluent

concentration (113 µg/L 2,4-DNT) was difficult to achieve. However, the system consistently removed more than 65 percent of the 2,4-DNT in the wastewater. An evaluation of the flows to the BWTP is required to determine if this removal rate (i.e., 65 percent reduction) would permit the BWTP to meet anticipated discharge standards.

A pretreatment system installed to intercept the wastewater released from the WD and WS operations could potentially intercept over 90 percent of the 2,4-DNT influent loading to the BWTP.[2] The remaining 2,4-DNT loading to the BWTP would be attributed to the solvent recovery and propellant coating operations. It is estimated that the WD and WS operations contribute less than 15 percent of the total wastewater flowing into the BWTP. Therefore, an 85 percent reduction of the concentration of 2,4-DNT would be anticipated due to dilution with non-DNT wastewaters upon entering the BWTP. As previously noted, the BWTP achieves reduction of 2,4-DNT concentrations as a result of aerobic biodegradation and possibly adsorption to solids which are removed from the system by sedimentation. The degree of treatment required by a pretreatment system to attain the 113 µg/L average and 285 µg/L peak discharge levels in the effluent of the BWTP is dependent upon the relative flow rates of DNT and non-DNT wastewaters, and the level of treatment achieved by the BWTP. Data are not available as to current and future flow rates and concentrations of 2,4-DNT in wastewaters at RAAP. Changing production levels and products and resultant changes in the wastewaters generated preclude a definitive calculation as to dilution rates and effectiveness of pretreatment by UV/OX. However, a UV/OX system alone does not appear to be capable of achieving concentrations of 113 µg/L DNT in treated WD wastewater.

UV/OX systems, in a wide variety of configurations to suit various process needs, are available through a number of commercial vendors. This technology has been implemented and proven effective and reliable on numerous wastewater streams. A relatively high degree of experience exists in the industry regarding the operation and maintenance of such systems.

Table 4-4
Analytical Results of UV/Oxidation Test Runs

Test Run No	Wastewater Flow Rate (gpm)	Retention Time* (min)	Analyte	SP-2 Influent (mg/L)	Average (mg/L)	SP-4 Cell 2 (mg/L)	Average (mg/L)	SP-6 Cell 4 (mg/L)	Average (mg/L)	SP-9 Effluent (mg/L)	Average (mg/L)
1	5	130.00	DNT	123.0 124.0 124.0	123.7	116.0 115.0 117.0	116.0	111.0 110.0 110.0	110.3	109.0 108.0 107.0	108.0
			Alcohol	103.0 99.9 104.0	102.3	101.0 104.0 102.0	102.3	103.0 95.1 103.0	100.4	94.5 94.4 102.0	97.0
			Ether	61.1 60.4 62.1	61.2	64.8 68.2 66.7	66.6	64.6 61.1 64.1	63.3	59.3 59.0 63.7	60.7
			COD	623.0 631.0 631.0	628.3	708.0 704.0 722.0	711.3	713.0 715.0 705.0	711.0	708.0 708.0 703.0	706.3
2	5	130.00	DNT	105.0 93.3 107.0	101.8	88.3 88.9 83.0	86.7	67.6 68.7 67.5	67.9	46.7 47.5 47.3	47.2
			Alcohol	104.0 97.4 104.0	101.8	76.5 72.1 78.0	75.5	51.3 51.0 48.2	50.2	31.4 31.0 33.1	31.8
			Ether	51.1 53.3 58.5	54.3	31.9 29.8 31.8	31.2	14.6 14.6 14.1	14.4	4.5 4.3 4.6	4.4
			COD	591.0 585.0 591.0	589.0	514.0 508.0 516.0	512.7	459.0 459.0 462.0	460.0	412.0 408.0 405.0	408.3
3	5	130.00	DNT	110.2 111.7 111.5	111.1	88.6 88.8 87.8	88.4	59.4 59.8 59.6	59.6	36.0 36.2 36.3	36.2
			Alcohol	98.0 99.0 91.0	96.0	79.0 72.0 70.0	73.7	44.0 43.0 43.0	43.3	25.0 23.0 24.0	24.0
			Ether	55.0 55.0 50.0	53.3	34.0 31.0 25.0	30.0	13.0 12.0 12.0	12.3	3.5 3.0 3.1	3.2
			COD	560.0 556.0 563.0	559.7	554.0 553.0 551.0	552.7	479.0 471.0 482.0	477.3	424.0 414.0 415.0	417.7
4	2.5	260.00	DNT	119.0 116.0 116.0	117.0	75.0 73.0 75.0	74.3	22.6 24.0 24.0	23.5	3.3 3.6 4.3	3.7
			Alcohol	90.0 96.0 94.0	93.3	57.0 58.0 58.0	57.7	18.0 19.0 20.0	19.0	3.2 3.1 3.3	3.2
			Ether	86.0 89.0 86.0	87.0	31.0 31.0 31.0	31.0	2.6 3.0 3.2	2.9	0.0 0.0 0.0	0.0
			COD	608.0 591.0 596.0	598.3	481.0 494.0 485.0	486.7	329.0 355.0 347.0	343.7	261.0 255.0 247.0	254.3

Table 4-4
Analytical Results of UV/Oxidation Test Runs

Test Run No	Wastewater Flow Rate (gpm)	Retention Time* (min)	Analyte	SP-2 Influent (mg/L)	Average (mg/L)	SP-4 Cell 2 (mg/L)	Average (mg/L)	SP-6 Cell 4 (mg/L)	Average (mg/L)	SP-9 Effluent (mg/L)	Average (mg/L)
5	1.5	433.33	DNT	113.0 112.0 112.0	112.3	83.0 81.0 81.0	81.7	52.0 52.0 52.0	52.0	34.0 34.0 33.0	33.7
			Alcohol	971.0 961.0 961.0	964.3	698.0 741.0 694.0	711.0	442.0 447.0 450.0	446.3	285.0 283.0 282.0	283.3
			Ether	75.0 75.0 73.0	74.3	24.0 26.0 24.0	24.7	5.4 5.3 5.3	5.3	1.3 1.3 1.3	1.3
			COD	2,750.0 2,650.0 2,700.0	2,700.0	1,925.0 2,675.0 2,550.0	2,383.3	2,250.0 2,225.0 2,350.0	2,275.0	1,925.0 1,950.0 2,000.0	1,958.3
6	2.5	260.00	DNT	64.0 64.0 65.0	64.3	51.0 48.0 48.0	49.0	32.0 32.0 24.0	29.3	21.0 22.0 21.0	21.3
			Alcohol	354.0 353.0 348.0	351.7	302.0 302.0 302.0	302.0	247.0 246.0 246.0	246.3	198.0 197.0 197.0	197.3
			Ether	40.0 42.0 38.0	40.0	31.0 31.0 29.0	30.3	16.9 16.5 16.9	16.8	8.8 8.7 8.6	8.7
			COD	1,029.0 1,018.0 1,040.0	1,029.0	980.0 990.0 1,008.0	992.7	899.0 915.0 912.0	908.7	836.0 834.0 842.0	837.3
7	2.5	260.00	DNT	67.0 61.0 66.0	64.7	48.0 46.0 49.0	47.7	31.0 33.0 33.0	32.3	20.0 19.0 19.0	19.3
			Alcohol	361.0 357.0 350.0	356.0	244.0 246.0 248.0	246.0	144.0 153.0 145.0	147.3	73.0 70.0 70.0	71.0
			Ether	40.0 45.0 44.0	43.0	18.6 18.8 18.5	18.6	5.8 6.1 5.8	5.9	1.5 1.5 1.3	1.4
			COD	990.5 988.0 997.0	991.8	916.5 921.0 927.5	921.7	781.5 773.5 793.5	782.8	663.0 664.5 673.5	667.0
8	2.5	260.00	DNT	59.7 63.0 58.8	60.5	27.4 27.6 27.0	27.3	9.0 9.0 8.3	8.8	1.6 1.7 1.6	1.6
			Alcohol	333.0 305.0 322.0	320.0	159.0 145.0 153.0	152.3	39.0 39.0 39.0	39.0	6.1 6.4 5.7	6.1
			Ether	34.0 21.0 30.0	28.3	8.2 7.3 7.9	7.8	0.0 0.0 0.0	0.0	0.39 0.46 0.42	0.42
			COD	982.0 965.0 956.0	967.7	863.0 858.0 860.0	860.3	642.0 634.0 650.0	642.0	473.0 471.0 468.0	470.7

			Time =	0 min.	120 min.	240 min.	360 min.	480 min.	600 min.	720 min.	
9	5.5	118.18	DNT	59.9	24.8	8.2	0.99	0.1	0	0	
			Alcohol	297	150	36	2.3	0	0	0	
			Ether	28	4.1	0	0.49	0	0	0	
			COD	948	773	619	495	330	179	55	

*- Based on 650 gallons of reactor volume

Table 4-5. Rate of reaction equations.

ZERO ORDER

$$-r_{DNT} = -\frac{dC_{DNT}}{dt} = k$$

Where: k = Reaction rate constant

C_{DNT} = DNT Concentration at time t

$C_{0\,DNT}$ = Initial DNT Concentration

Integrating,

$$C_{0\,DNT} - C_{DNT} = kt$$

A plot of DNT concentrations versus time (C_{DNT} vs t) will be a straight line with:

y-intercept = $C_{0\,DNT}$, and

slope = k

FIRST ORDER

$$-r_{DNT} = -\frac{dC_{DNT}}{dt} = kC_{DNT}$$

Integrating,

$$\ln\left(\frac{C_{DNT}}{C_{0\,DNT}}\right) = -kt$$

A plot of $\ln\left(\dfrac{C_{DNT}}{C_{0\,DNT}}\right)$ versus time will be a straight line passing through the origin and with slope = k

SHIFTING ORDER (ZERO TO FIRST ORDER REACTION)

$$-r_{DNT} = -\frac{dC_{DNT}}{dt} = \frac{k_1 C_{DNT}}{1 + k_2 C_{DNT}}$$

Where: k_1 = First order reaction rate constant

k_2 = Zero order reaction rate constant

Integrating,

$$\ln\left[\frac{C_{0\,DNT}\,/\,C_{DNT}}{C_{0\,DNT} - C_{DNT}}\right] = -k_2 + \frac{k_1 t}{C_{0\,DNT} - C_{DNT}}$$

A plot of $\ln\left(\dfrac{C_{DNT}}{C_{0\,DNT}}\right)$ versus $\dfrac{k_1 t}{C_{0\,DNT} - C_{DNT}}$ will be a straight line passing through $-k_2$ and with slope = k_1

Table 4-6
Summary of Analytical Results and 2,4-DNT Destruction Efficiencies During UV/Oxidation Test Runs

Run No	Wastewater Flow Rate (gpm)	Sampling Point	Time (min)	DNT Conc. (mg/L)	Alcohol Conc. (mg/L)	Ether Conc. (mg/L)	COD Conc. (mg/L)	pH	DNT Destruction	Rate Equation
1	5	Influent	0.00	123.7	102.3	61.2	628.3	7.12		
		Cell 2	32.50	116.0	102.3	66.6	711.3	7.11		
		Cell 4	75.83	110.3	100.4	63.3	711.0	7.05		
		Effluent	130.00	108.0	97.0	60.7	706.3	6.96	13%	Zero-order
2	5	Influent	0.00	101.8	101.8	54.3	589.0	7.03		
		Cell 2	32.50	86.7	75.5	31.2	512.7	5.14		
		Cell 4	75.83	67.9	50.2	14.4	460.0	4.24		
		Effluent	130.00	47.2	31.8	4.4	408.3	3.90	54%	Zero-order
3	5	Influent	0.00	111.1	96.0	53.3	559.7	6.93		
		Cell 2	32.50	88.4	73.7	30.0	552.7	5.52		
		Cell 4	75.83	59.6	43.3	12.3	477.3	4.30		
		Effluent	130.00	36.2	24.0	3.2	417.7	3.75	67%	Zero-order
4	2.5	Influent	0.00	117.0	93.3	87.0	598.3	3.97		
		Cell 2	65.00	74.3	57.7	31.0	486.7	4.65		
		Cell 4	151.67	23.5	19.0	2.9	343.7	3.55		
		Effluent	260.00	3.7	3.2	0.0	254.3	3.25	97%	Shifting-order
5	1.5	Influent	0.00	112.3	964.3	74.3	2700.0	6.73		
		Cell 2	108.33	81.7	711.0	24.7	2383.3	4.13		
		Cell 4	252.78	52.0	446.3	5.3	2275.0	3.47		
		Cell 5	325.00	43.0	368.7	2.7				
		Effluent	433.33	33.7	283.3	1.3	1958.3	3.18	70%	Zero-order
6	2.5	Influent	0.00	64.3	351.7	40.0	1029.0	6.76		
		Cell 2	65.00	49.0	302.0	30.3	992.7	5.22		
		Cell 4	151.67	29.3	246.3	16.8	908.7	4.62		
		Effluent	260.00	21.3	197.3	8.7	837.3	4.29	67%	Shifting-order
7	2.5	Influent	0.00	64.7	356.0	43.0	991.8	6.63		
		Cell 2	65.00	47.7	246.0	18.6	921.7	4.59		
		Cell 4	151.67	32.3	147.3	5.9	782.8	4.04		
		Effluent	260.00	19.3	71.0	1.4	667.0	3.72	70%	Zero-order
8	2.5	Influent	0.00	60.5	320.0	28.3	967.7	6.05		
		Cell 2	65.00	27.3	152.3	7.8	860.3	4.11		
		Cell 4	151.67	8.8	39.0	0.0	642.0	3.66		
		Effluent	260.00	1.6	6.1	0.4	470.7	3.44	97%	Shifting-order
9	5.5	Cell 6	0.00	59.9	297	28	948	5.58		
		Cell 6	120.00	24.8	150	4.1	773	4.17		
		Cell 6	240.00	8.2	36	0	619	3.74		
		Cell 6	360.00	0.99	2.3	0.49	495	3.48		
		Cell 6	480.00	0.1	0	0	330	3.42		
		Cell 6	600.00	0	0	0	179	3.33		
		Cell 6	720.00	0	0	0	55	3.16	100%	First-order

Figure 4-3
DNT Concentration vs. Retention Time
Runs 1, 2, and 3

Wastewater Flow Rate = 5 gpm
Total Oxidant Dosage:
  Run 1 = 439 mg/L Ozone Only
  Run 2 = 415 mg/L H_2O_2 Only
  Run 3 = 420 mg/L Ozone/H_2O_2
UV Lamp Intensity = 100 %

DNT Concentration (mg/L)

Time (minutes)

Run 1   Run 2   Run 3
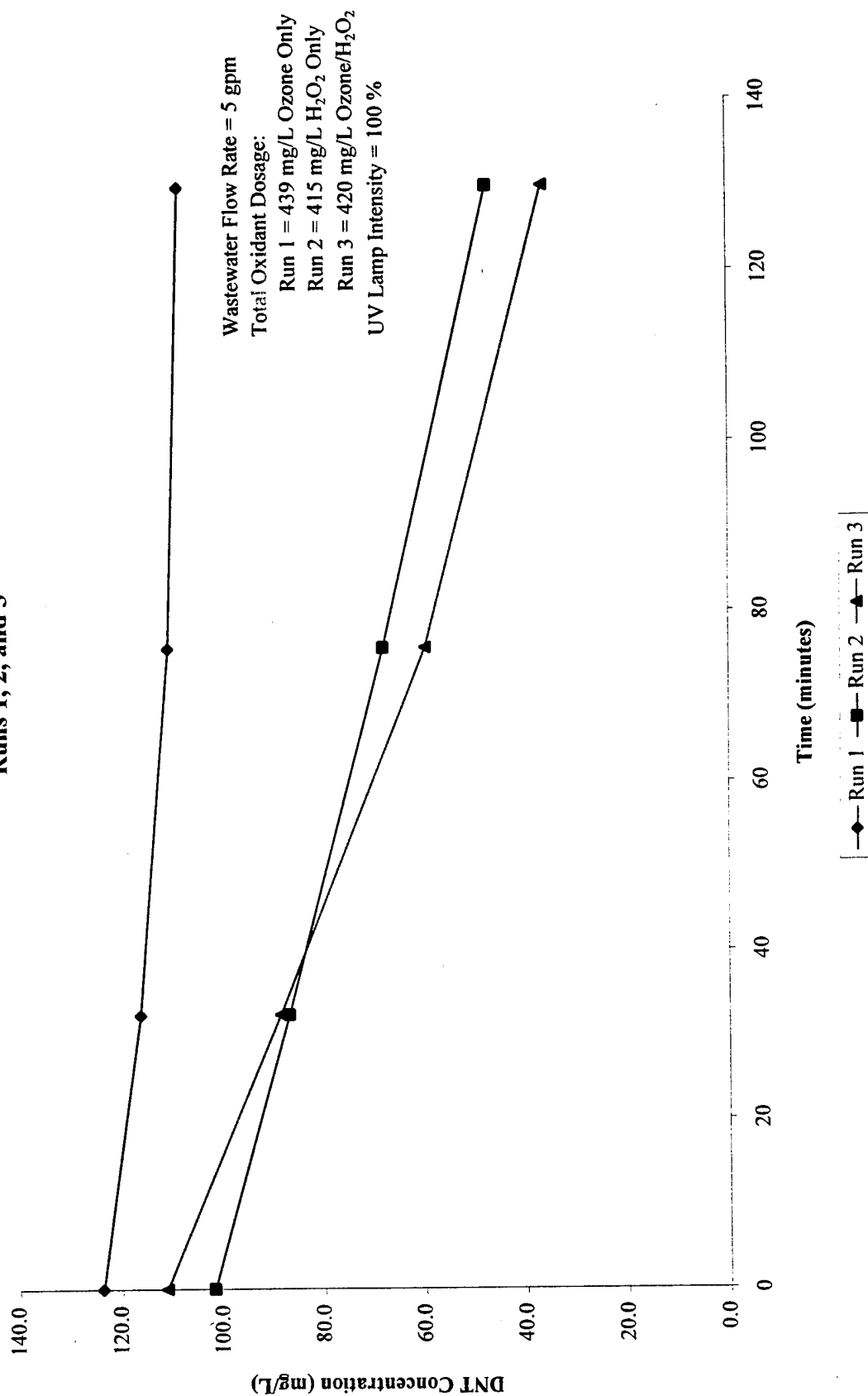
Figure 4-4
DNT Concentration vs. Retention Time
Run 4

Wastewater Flow Rate = 2.5 gpm
Total Oxidant Dosage = 839 mg/L
Oxidant Type = Ozone and H_2O_2
UV Lamp Intensity = 100 %

Run 4

DNT Concentration (mg/L)

Time (minutes)
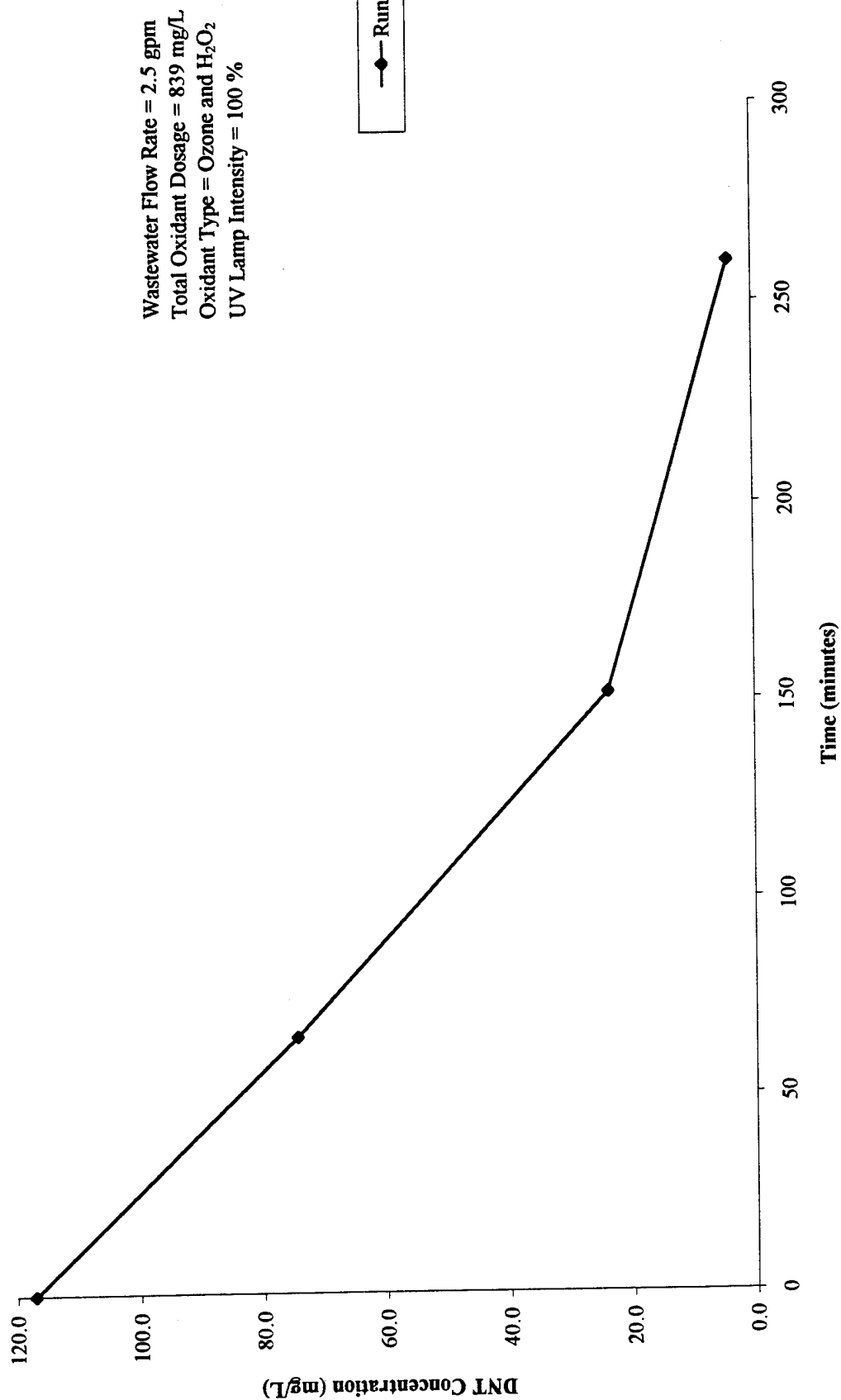
Figure 4-5
DNT Concentration vs. Retention Time
Run 5

Wastewater Flow Rate = 1.5 gpm
Total Oxidant Dosage = 1,870 mg/L
Oxidant Type = Ozone and H_2O_2
UV Lamp Intensity = 100 %

Run 5

Time (minutes)

DNT Concentration (mg/L)
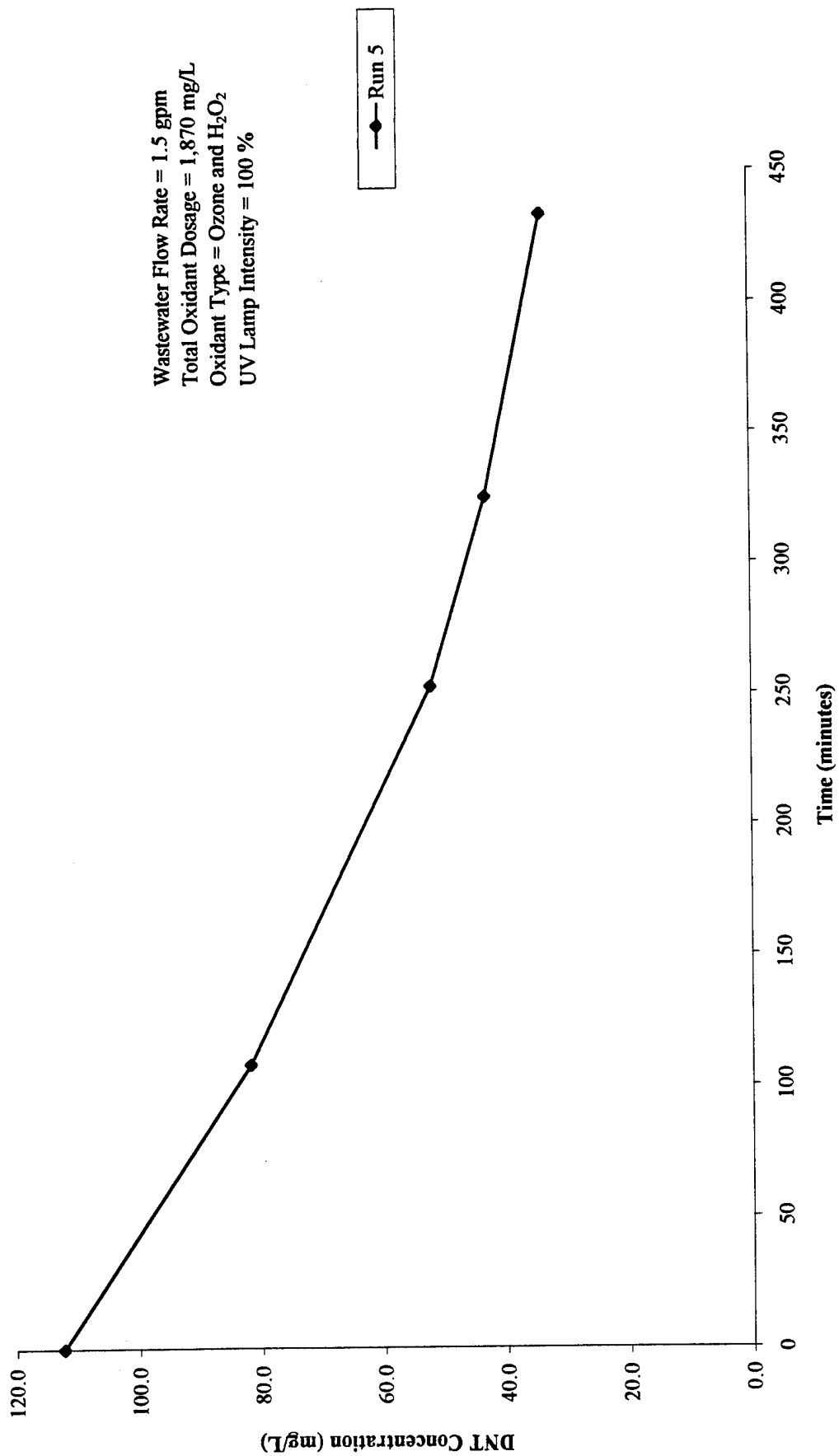
Figure 4-6
DNT Concentration vs. Retention Time
Run 6

Wastewater Flow Rate = 2.5 gpm
Total Oxidant Dosage = 420 mg/L
Oxidant Type = Ozone and H_2O_2
UV Lamp Intensity = 100 %

Run 6

Time (minutes)

DNT Concentration (mg/L)
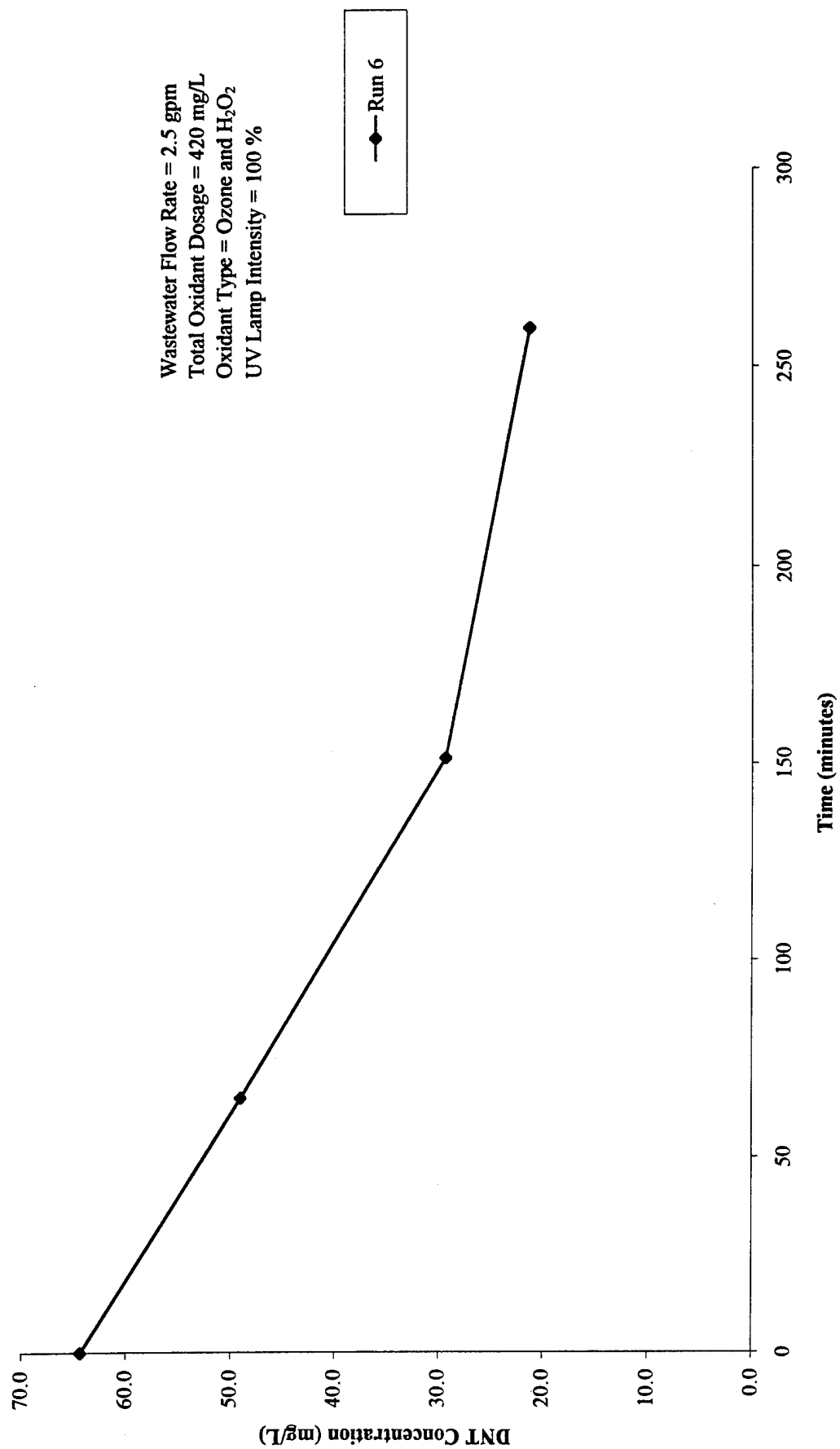
Figure 4-7
DNT Concentration vs. Retention Time
Run 7

Wastewater Flow Rate = 2.5 gpm
Total Oxidant Dosage = 839 mg/L
Oxidant Type = Ozone and H_2O_2
UV Lamp Intensity = 50 %

Run 7
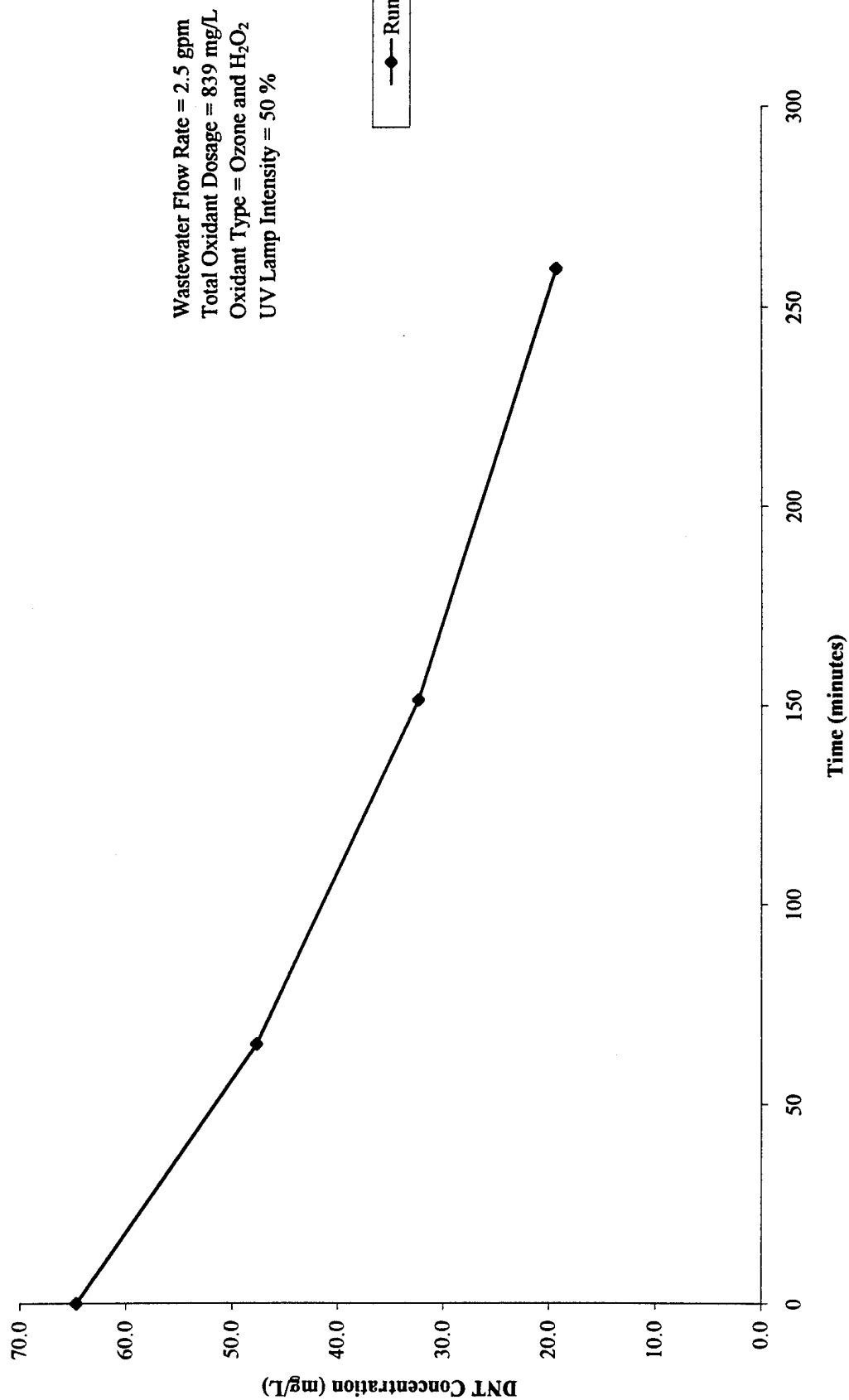
Figure 4-8
DNT Concentration vs. Retention Time
Run 8

Wastewater Flow Rate = 1.5 gpm
Total Oxidant Dosage = 1,399 mg/L
Oxidant Type = Ozone and H_2O_2
UV Lamp Intensity = 100 %

Run 8

DNT Concentration (mg/L)

Time (minutes)
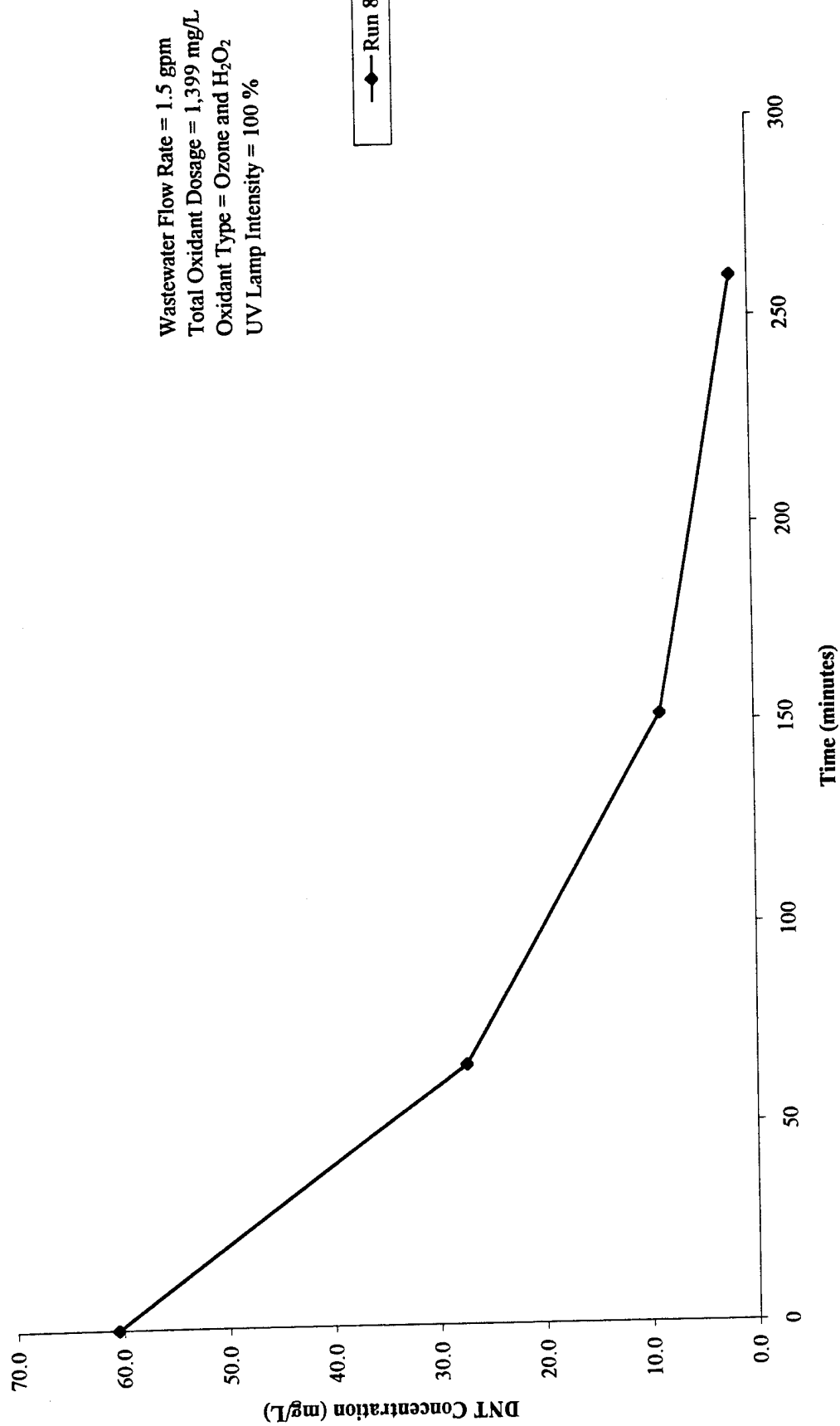
Figure 4-9
DNT Concentration vs. Retention Time
Run 9

Wastewater Flow Rate = 5 gpm
Total Oxidant Dosage = 2,324 mg/L
Oxidant Type = Ozone and H_2O_2
UV Lamp Intensity = 100 %
Batch Operation
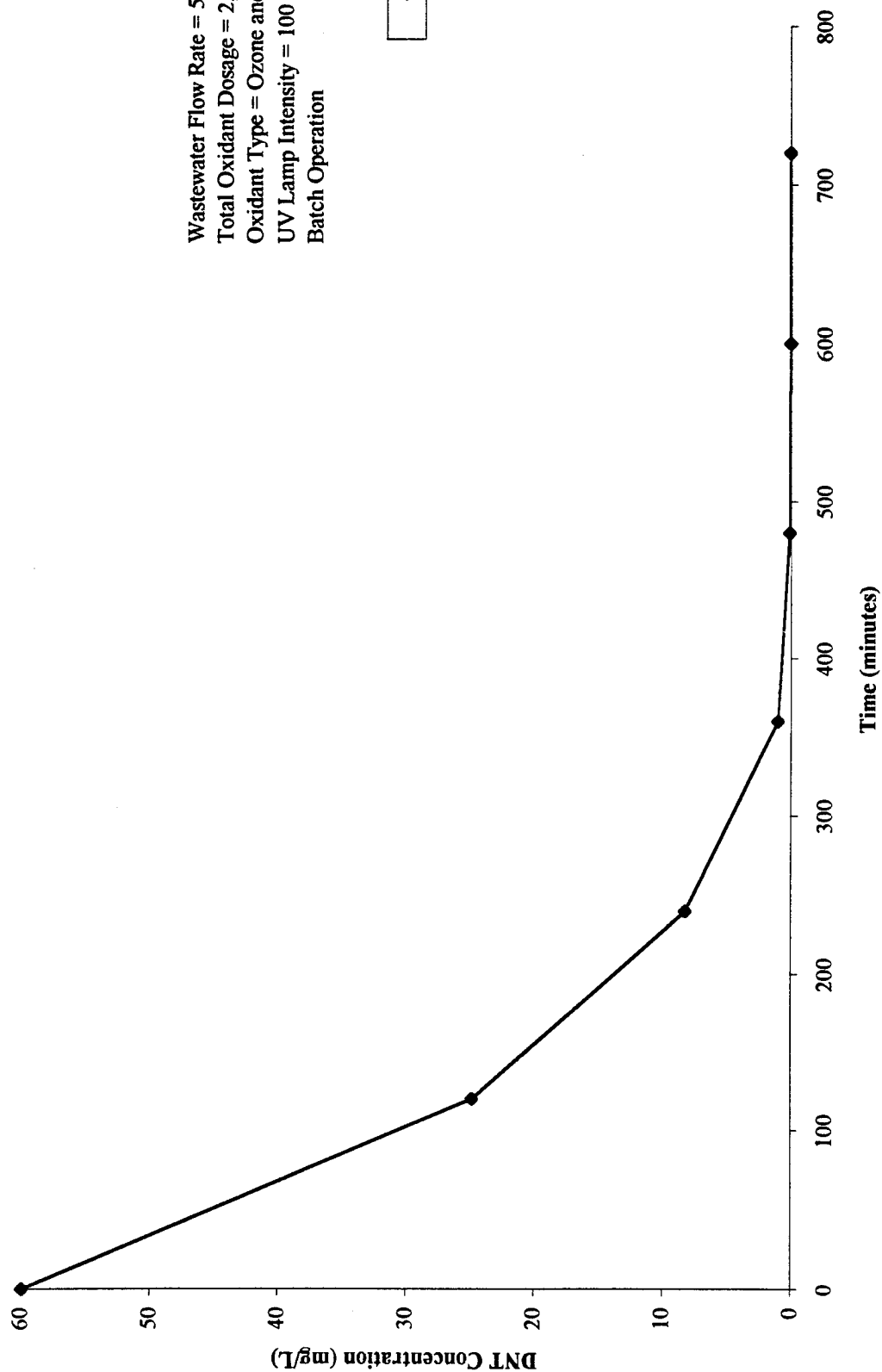
5.0 DEMONSTRATION OF AnFBR/RBC

The equipment and methodology used, and the results of the pilot-scale demonstration of AnFBR and RBC treatment of WD wastewater at the RAAP are summarized in this section.

5.1 AnFBR and RBC Theory

The AnFBR technology has been studied by others for treatment of industrial wastewaters such as those associated with coal gasification, manufacture of thermoplastic resin, and wood treating processes (Section 3). The results of bench-scale studies conducted by the USACERL to assess the use of AnFBR specifically for removal of 2,4-DNT from wastewaters at RAAP concluded that this technology is a potentially viable alternative.[9,20] These studies indicate that 2,4-DNT can be reduced to DAT under methanogenic conditions if a primary growth substrate, such as ethanol, is present. The DAT formed by this degradation is resistant to further anaerobic transformation but is readily mineralized under aerobic conditions such as are present in the BWTP. Thus, this demonstration program was configured to include an AnFBR followed by an RBC. This treatment train was used to demonstrate anaerobic conversion of 2,4-DNT to DAT in the AnFBR and subsequent aerobic mineralization of DAT by the RBC.

An AnFBR system consists of a vertical tank containing GAC. Wastewater is fed to the reactor from the bottom at sufficient velocity to fluidize the bed and expand its volume by a factor of approximately 1.5. The fluidized bed of GAC provides two functions in an AnFBR system, first it provides physical support for attachment and growth of bacteria that are capable of assimilating and degrading organics present in the influent stream. In this function, the GAC provides large surface area which can support the biomass in a compact reactor. Second, the GAC absorbs slug or surge loadings of 2,4-DNT such as may be present during startup or as observed during propellant production batch operations at RAAP. During periods of low influent flows or low concentrations of 2,4-DNT, the 2,4-DNT adsorbed on the GAC desorbs and is subsequently degraded by the bacteria, thus regenerating the carbon bed. The contact time required for effective treatment is dependent on the concentration of 2,4-DNT and the presence of other compounds competing for absorption sites and is one of the variables that was evaluated during the demonstration. As necessary, biomass and spent GAC can be removed from the reactor during operation.

5.2 Selection of Equipment

Based on the results of the previous USACERL study, vendors of fluidized bed bioreactors were contacted to identify available equipment. Concurrent with the initiation of this effort USACERL initiated acquisition of a pilot-scale AnFBR system for use under a separate research and development program. Subsequently, a pilot-scale AnFBR unit was procured by USACERL and made available for this study. The system used was capable of operating at hydraulic flow rates up to 30 gpm; however, the maximum flow rate through the system is limited by the residence time required for treatment of the wastewater. During the demonstration the forward flow rate was on the order of 0.4 gpm to 2 gpm.

A pilot-scale RBC unit, which had been used previously by Alliant during the design of the BWTP, was used for the demonstration. The effluent flow from the AnFBR was the influent to the RBC. Therefore, the flowrates used during the RBC demonstration were limited to those used during the tests of the AnFBR system.

5.3 Equipment Description and Operation

The AnFBR system used during the demonstration (Figure 5-1) was manufactured by Envirex, Ltd.. The system, a Model 30 modified for anaerobic operation, consisted of a 15-foot tall, 20-inch diameter reactor column, an autocontroller and data logger, nutrient and pH buffer tanks and pumps, forward flow and recycle pumps, and other features as described below. The reactor column had a bed volume of approximately 187 gallons and, was initially loaded with approximately 380 lbs of carbon (Calgon MRX-P® 10x30, or equivalent). During startup, carbon fines were siphoned from the system which reduced the amount of carbon in the reactor by about 10 percent. During operation of an AnFBR system, biomass growing on carbon particles reduces the effective particle density eventually causing the particle to float to the top of the water in the reactor. An overflow pipe was located in the reactor at a height of 11.5 feet. As rising carbon particles reached this height they overflowed from the reactor and drained to a settling tank. After settling, the carbon particles were pumped through a pinch valve where biomass was sheared from the carbon. This carbon was then returned to the reactor and the biomass was wasted from the system.
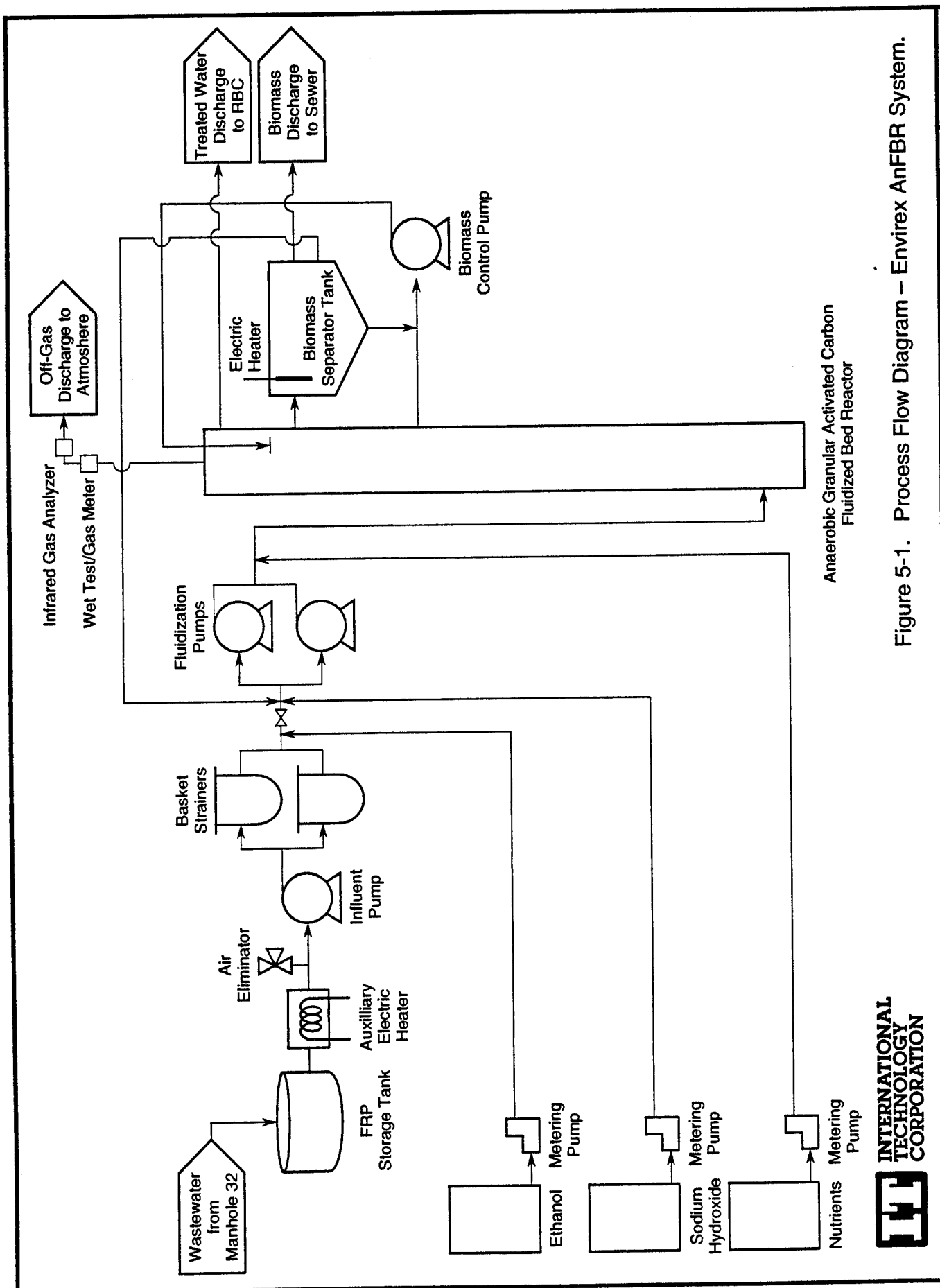
Figure 5-1. Process Flow Diagram – Envirex AnFBR System.

Off-Gas Discharge to Atmoshere

Treated Water Discharge to RBC

Biomass Discharge to Sewer

Infrared Gas Analyzer

Wet Test/Gas Meter

Electric Heater

Biomass Separator Tank

Biomass Control Pump

Anaerobic Granular Activated Carbon Fluidized Bed Reactor

Fluidization Pumps

Basket Strainers

Influent Pump

Air Eliminator

Auxilliary Electric Heater

FRP Storage Tank

Wastewater from Manhole 32

Ethanol

Metering Pump

Sodium Hydroxide

Metering Pump

Nutrients

Metering Pump

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In order to ensure biological growth, the Envirex system included systems for adding nutrients (trace elements, phosphorus, etc.), a supplemental carbon source (ethanol), and a pH control buffer solution (sodium hydroxide). The nutrient solution was metered into the influent line. The ethanol solution, which was also metered into the influent line, served as a co-substrate for 2,4-DNT transformation. A sodium hydroxide solution was fed into the recycle line to control the pH in the reactor. Without control, the reactor pH would fall as a result of the production of organic acids when the methane producing bacteria cannot degrade at the same rate as acid producing bacteria. Methane production is accomplished in a two step process with two sets of bacteria involved. Under steady-state conditions, pH control is not necessary, but under variable industrial wastewater conditions, pH control is necessary for periods of transition.

A programmable logic controller (PLC) was added to the system to monitor operating parameters including the levels of solution in the nutrient and sodium hydroxide tanks, the pH in the reactor, the dissolved oxygen content, temperature, and recycle and forward flow flowrates. In the event of a system malfunction, the PLC was programmed to shut down major system components and automatically switch the system into by-pass (i.e., recycle) mode. The PLC also activated an autodialer to notify an operator of the shutdown condition. Data monitored by the PLC were stored in a data collector that permitted remote retrieval via a telephone connection. The Model 30 also included an air compressor that provided the air necessary to operate the air-controlled valves, an infrared gas monitor that measured the carbon dioxide and methane content in the reactor off-gas, and a wet test meter to monitor the volume of gas produced.

All biological treatment systems require a period of acclimation for the biomass. During start-up of the AnFBR, a seed culture of bacteria is grown into a viable biomass. Wastewater is then gradually introduced in a manner that avoids shocking the system which can inhibit or even kill the biomass. The operating conditions used for the startup and acclimation of the Envirex system are shown in Table 5-1. Initially, the system was started on an influent feed of clean plant water dosed with ethanol and a nutrient solution to provide metabolites necessary for growth of the microorganisms. During startup, the ethanol feed was adjusted to maintain a COD loading rate of approximately 10 kg COD/m^3 GAC per day (approximately 1,560 mg/l ethanol at a flowrate of 0.4 gpm). Based on the experience of the vendor, it was anticipated that a period of

Table 5-1

Operating Conditions During Startup and Acclimation of the AnFBR and RBC

	AnFBR Influent						AnFBR Effluent						RBC Effluent						Alcohol Feed, (mL/min)	Nutrient Feed, (mL/min)
Date	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD*, (mg/L)	pH, (SU)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	pH, (pH Units)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	pH, (pH Units)		
12/1/94	ND	ND	236	22.0	339	7.57	ND	ND	240	23.0	336	7.49	ND	ND	8.2	ND	144	7.60	NA	NA
12/2/94	ND	ND	63	12.3	94	7.31	ND	ND	64	11.5	91	7.27	ND	ND	0.82	1.3	68	7.23	NA	NA
12/5/94	ND	ND	31	1.5	63	7.63	ND	ND	29	1.3	75	7.64	ND	ND	5.2	3.7	232	6.82	0	1.3
12/6/94	ND	13	ND	ND	92	7.60	ND	ND	ND	ND	67	7.80	ND	ND	ND	ND	60	7.08	2.2	2.01
12/7/94	276	ND	479	3.5	1,151	6.83	295	ND	468	1.6	1,175	6.87	124	ND	283	3.0	556	7.52	18.8	0.7
12/8/94	221	ND	413	1.7	947	8.81	214	ND	423	1.7	946	7.59	49	ND	291	6.2	487	7.32	5.08	1.2
12/9/94	19	ND	373	3.7	400	6.71	18	ND	382	3.2	385	6.63	ND	ND	7.3	ND	99	7.23	2.25	1.37
12/12/94	ND	ND	ND	ND	52	8.03	ND	ND	ND	ND	44	8.00	ND	ND	ND	ND	46	7.38	0	3.05
12/13/94	186	ND	361	ND	795	7.50	185	ND	371	ND	791	7.53	53	ND	240	0.13	386	7.20	NA	NA
12/14/94	22	ND	308	1.8	367	8.29	23	ND	312	0.9	387	8.14	ND	ND	1.1	ND	77	7.23	2.2	2.01
12/15/94	536	ND	463	ND	1,693	7.33	515	ND	472	ND	1,651	7.77	247	ND	282	1.3	934	7.24	15.8	1.9
12/16/94	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	7.9	4.1
12/19/94	50	ND	87	0.9	231	7.29	21	ND	73	ND	143	7.73	NA	NA	NA	ND	62	6.96	NA	NA
12/20/94	891	ND	633	ND	2,525	7.96	871	ND	655	ND	2,300	7.18	551	ND	331	0.5	1,628	7.55	16.1	3.9
12/21/94	1297	ND	648	2.0	3,225	7.27	1,250	ND	672	1.2	3,525	7.46	1063	ND	450	4.9	2,500	7.14	9.4	4.9
12/22/94	1524	ND	722	1.0	3,900	7.19	1,563	ND	735	0.6	3,950	7.33	1192	ND	549	21.0	3,375	7.14	NA	NA
12/23/94	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12/27/94	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12/28/94	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12/29/94	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
12/30/94	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
1/1/95	577	ND	631	3.3	2,050	7.10	594	ND	629	2.0	2,275	7.26	20	21	397	8.9	1,825	5.91	9.4	4.9
1/3/95	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	10.5	5.9
1/4/95	751	ND	745	3.4	2,550	7.84	763	ND	753	3.2	2,575	7.44	No sample	No sample	No sample	No sample	No sample	No sample	10.9	5.8
1/5/95	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	??
1/6/95	842	ND	730	6.1	12,800	8.09	842	ND	761	5.0	13,300	6.93	204	ND	510	7.1	12,175	5.96	NA	NA
1/9/95	No sample	No sample	No sample	No sample	No sample	No sample	846	ND	1,057	4.7	12,735	7.30	3.5	ND	67	0.4	11,675	7.41	NA	NA
1/10/95	856	ND	1,286	6.4	3,350	7.17	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	NA	NA
1/11/95	488	ND	536	3.4	4,038	7.28	505	ND	570	2.5	4,263	7.20	No sample	No sample	No sample	No sample	No sample	No sample	NA	NA
1/12/95	290	ND	435	5.2	1,072	7.54	283	ND	432	3.8	1,091	7.18	No sample	No sample	No sample	No sample	No sample	No sample	NA	NA
1/13/95	566	ND	489	6.9	1,888	7.88	559	ND	508	6.3	1,788	7.44	1.8	ND	159	8.3	508	7.20	4	4.7
1/16/95	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	No sample	NA	NA
1/17/95	703	ND	524	8.5	2,375	7.01	691	ND	532	7.4	2,275	6.03	57	ND	248	12.3	1,700	7.40	12.5	3.2
1/18/94	684	ND	546	10.4	2,000	6.43	692	ND	551	10.5	2,125	6.67	49	ND	262	12.2	1,540	6.11	13.1	5.3
1/19/95	707	ND	712	14.0	2,463	7.13	718	ND	752	14.0	2,413	7.30	18	ND	348	17.0	1,900	6.40	11.8	5.9
1/20/95	787	1.2	771	14.6	2,400	6.61	727	ND	790	13.8	2,413	6.64	12.2	ND	355	20.9	1,850	6.40	9.7	4.5
1/23/95	618	1.7	804	15.9	2,275	7.26	621	Trace	804	16.2	2,438	6.96	ND	ND	355	18.7	1,488	6.83	7.06	4.4
1/24/95	623	1.2	700	13.1	2,138	6.95	630	Trace	713	13.7	2,250	7.07	15.6	ND	298	20.3	1,488	6.99	9.11	3.4
1/25/95	518	2.7	619	14.6	2,088	6.77	529	1.5	632	13.6	2,150	6.79	7.7	ND	250	16.2	1,200	6.77	5.7	4.4
1/26/95	532	2.6	627	12.5	1,675	6.89	525	1.7	630	11.7	1,963	6.96	12	ND	267	14.5	1,288	7.06	6.8	3.2
1/27/95	536	4.5	629	12.8	2,000	6.88	531	3.5	660	12.0	1,688	6.74	4.7	ND	295	14.1	1,088	6.39	7.2	4.6
1/30/95	590	7.3	815	10.2	NA	6.94	583	6.5	850	10.3	2,038	6.98	5.2	ND	445	14.1	1,475	6.80	7.7	5.4

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

4 to 6 weeks of operation under the startup conditions would be required to establish a viable biomass. However, due to operational problems associated with the reactor, the startup time extended to approximately 14 weeks. During this period the reactor was inoculated with anaerobic sludge obtained from a local POTW on three occasions. Subsequently, WD wastewater was pumped from the storage tank and slowly introduced to the system to allow the system to acclimate to the WD wastewater.

Based on initial analysis of the WD wastewater, it was anticipated that sufficient ethanol was present in the WD wastewater to serve as a co-substrate for 2,4-DNT degradation. Therefore, ethanol feed to the influent was gradually decreased. The wastewater feed to the system was controlled to maintain a COD loading rate of between 5 and 10 kg COD/m^{3}GAC/day.

Following any change in operating conditions, the system was operated at the new conditions for a sufficient time to allow it to return to a steady-state (i.e., to reacclimate). For the purpose of this demonstration, a steady-state was defined as when, over a period of three consecutive days, gas production rates and buffer solution flow rates remained constant, and consecutive daily paired influent/effluent samples indicated steady DNT removal rates. When these conditions were met, the test run was initiated. Each test run lasted a period of 2 to 10 days during which operational conditions were monitored extensively and multiple influent and effluent samples were taken for analysis.

The pilot-scale RBC unit used during the demonstration was previously used at RAAP in the mid-1970s, to establish the operating and design parameters for the existing BWTP. Two previous reports describe this unit: "Biological Pilot Plant Study at Radford Army Ammunition Plant," (Hercules, October, 1976), and "Evaluation of an Anaerobic Rotating Biological Contactor System for Treatment of a Munition Wastewater Containing Organic and Inorganic Nitrates," (Hercules). These reports detail the use of the pilot-scale RBC in both the aerobic and anaerobic modes. A smaller RBC (9-in. diameter discs) was used in previous bench-scale studies at RAAP[2]. The results of these studies were used to establish the operating conditions for the RBC used in this demonstration.

The pilot-scale RBC unit was a 0.5 m "Bio-Surf®" pilot unit produced by Autotrol Corporation. Overall, the unit measured 72 in. long, 28 in. wide, and 24 in. high. Its four cells were separated by removable bulkheads. Each cell contained a bank of nine 18-5/8 in. diameter corrugated polyethylene discs with a combined surface area of 250 ft². Influent to the RBC entered the first cell and the followed a serpentine path to each successive cell. A tilt pipe in the fourth cell was used to control the depth of the wastewater in the unit. The tilt pipe was positioned so that approximately 35 percent of the discs were submerged. At this depth, the volume of the unit was approximately 34 gallons. Based on the manufacturer's specifications, this unit can be operated at flow rates up to 3,150 gpd (hydraulic loading of 12.6 gpd/ft²), or 2.19 gpm.

A 25 gallon surge/aeration tank was installed in the line between the Envirex Model 30 and the RBC system. This allowed flowrates less than or equal to the flowrates of the Envirex system to be tested in the RBC. Additionally, the tank could be fed directly from the 20,000 gallon storage tank or be filled with plant water during periods when the Envirex system was not operating. Most importantly the surge/aeration tank facilitated aeration of the anaerobic effluent from the Envirex system.

As with the Envirex Model 30, the RBC system required an acclimation time for the establishment and growth of microbes on the discs that could degrade the DAT and other organic compounds present in the effluent from the Envirex system. Initially two to five gallons of RBC biomass was obtained from the BWTP and used to inoculate the system. A flowrate of 0.4 gpm of effluent from the AnFBR system provided adequate nutrients for the RBC biomass during the acclimatization period. Approximately two weeks were required for a sustainable colony of microbes to become established. The RBC system was considered to be acclimated when it achieved a constant COD removal rate.

An air-driven motor rotated the RBC discs at a rate of approximately 12 rpm. This rotation rate was selected based on previous reports and on the industry standard tip speed of approximately 1 ft/sec. Adherence of biomass to the disk and the propensity for sloughing is a function of tip speed. Full-scale RBC units with 12-foot diameter discs frequently rotate at about 1-1/2 rpm to maintain a tip speed of 1 ft/sec. This difference in rotation rates between pilot-scale and full-scale systems can introduce difficulties in scale-up design because the time that a disc is submerged and because the amount of oxygen available to the microbes varies with rotation rates. This is an inherent difficulty associated with pilot-scale testing of RBCs.

submerged and because the amount of oxygen available to the microbes varies with rotation rates. This is an inherent difficulty associated with pilot-scale testing of RBCs.

A simplified process flow diagram for the AnFBR/RBC demonstration system is shown in Figure 5-2. WD water from MH32 was fed to the 20,000-gallon closed-top fiberglass tank for temporary storage. This provided capacity that permitted a continuous feed of wastewater to the demonstration equipment. The stored wastewater was mixed using a centrifugal pump that was run intermittently during the demonstration. This pump circulated water from the bottom to the top of the storage tank. Data obtained during the demonstration indicated that this did not cause any appreciable decrease in alcohol concentration due to volatilization. Water was pumped from the storage tank to the AnFBR system where a strainer removed solids. Treated effluent from the AnFBR/RBC system was discharged by gravity to MH32, at a location downstream of the collection point for the influent. Figure 5-2 also indicates the locations for sample acquisition. Samples were collected from the storage tank, at the inlet (SC2) and outlet (SC3) of AnFBR and at the discharge of the RBC system.

5.4 Demonstration Methodology

As determined by previous bench-scale studies conducted by USACERL and USAEC, the critical operating parameters for the Envirex system are retention time, temperature, pH, and nutrient addition rate. Operational conditions that were used to evaluate these parameters during the demonstration are shown in Table 5-2. A discussion of the importance of each of these parameters is presented below.

Retention Time

The AnFBR system removes 2,4-DNT from wastewater through anaerobic transformation. As demonstrated by the previous bench-scale studies, the efficiency of 2,4-DNT removal is dependent on the retention time of the wastewater in the system and the concentrations of 2,4-DNT and ethanol in the WD wastewater. Due to the high rate of recycle flow in the Envirex system (30 gpm), the solids retention time of the wastewater is different from the hydraulic retention time. The solids retention time can be calculated based on the influent wastewater flowrate and the rate of recycle.
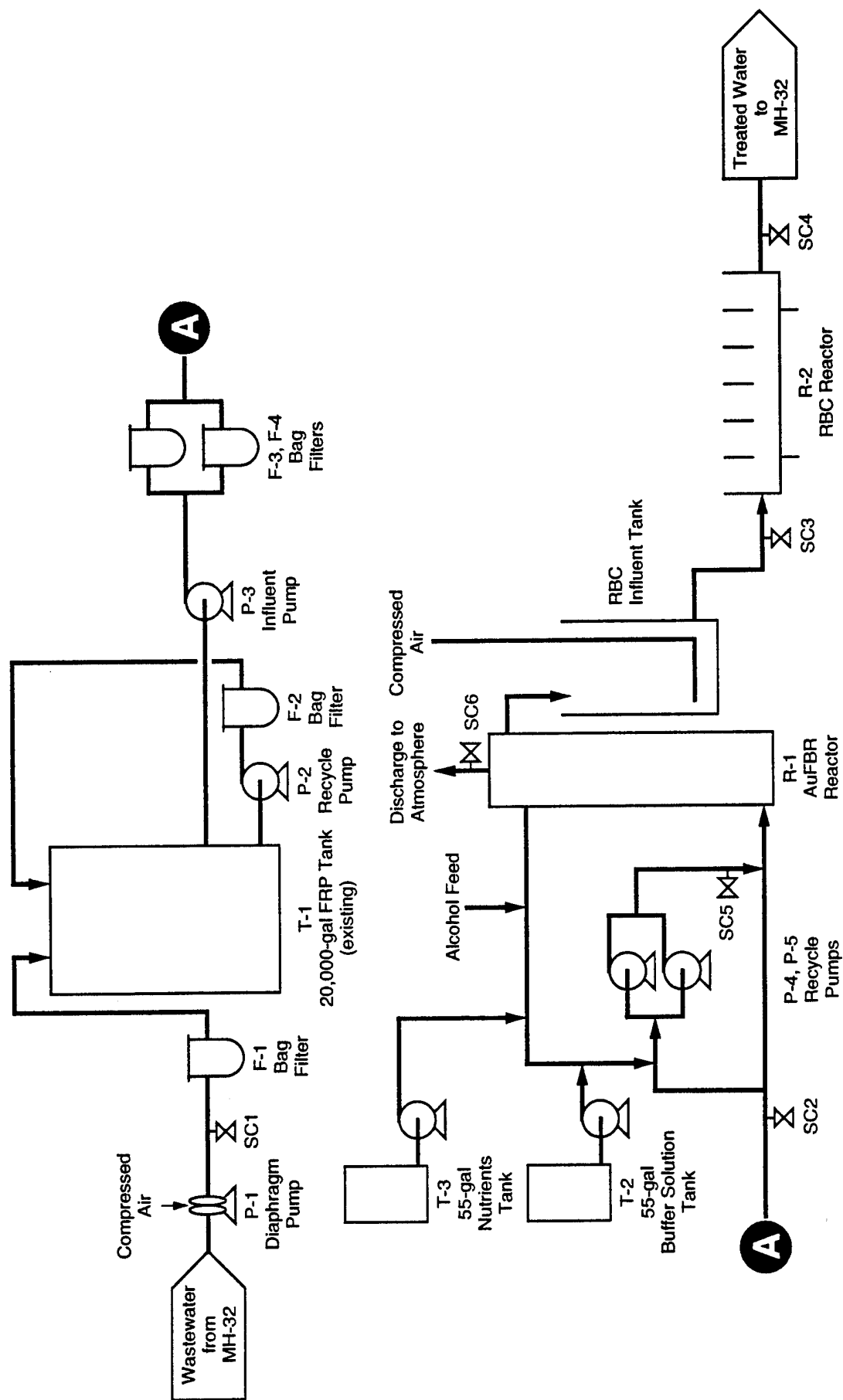
Figure 5-2. Process flow diagram – AnFBR/RBC Pilot-Test System.

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Table 5-2
Operational Conditions During the AnFBR Demonstration

Test Run No.	pH	Organic Loading Rate (OLR) (kg-COD/m³/day)	Temperature (°F)	Wastewater Flowrate (gpm)	Retention Time (hrs)
1	6.8-7.0	10	95	0.4	7.8
2	6.8-7.0	5	95	0.4	7.8
3	6.8-7.0	2.5	95	0.4	7.8
4	6.8-7.0	4.3	95	0.8	3.9
5	6.8-7.0	6.4	95	0.8	3.9
6	6.8-7.0	5	95	0.8	3.9
7	6.8-7.0	11	95	1.2	2.6
8	6.8-7.0	24	95	2	1.6

During the previous USACERL bench-scale study, a hydraulic retention time of 16 hours achieved effective removal of DNT. However, to maintain sufficient organic loading to the reactor, an influent wastewater flow rate (i.e., forward flow rate) and recycle flow rate of 0.4 and 30 gpm, respectively, resulted in a 7.8 hour hydraulic retention time. During successive test runs, the effect of hydraulic retention time was evaluated by altering the influent flowrate. For example, increasing the influent flowrate by 50 percent from the initial rate resulted in a hydraulic retention time of 3.9 hrs. The Envirex system was evaluated at the flowrates shown in Table 5-2. The retention time and the COD/DNT ratio were calculated from the flowrates and the composition of the influent wastewater.

Temperature

Temperature is a controlling or limiting factor in any biological system. Extreme temperatures inhibit bioactivity. Typical anaerobic biosystems operate at peak efficiency at a temperature of approximately 95°F. The WD wastewater has a temperature of approximately 150°F at its point of discharge from the WD building but cools as it flows through the sewer and during storage in the feed tank. The temperature of the influent wastewater was monitored, but not controlled, during the initial tests. The temperature in the reactor was to be maintained at 95°F. The system was modified with the installation of an auxilliary heater in the influent line to maintain the temperature in the reactor.

pH

Anaerobic bioactivity results in production of organic acids that decrease the pH of the operating system. The biological organisms may be adversely impacted by a decrease in pH; therefore, pH control is necessary for efficient operation of the Envirex system. A solution of sodium hydroxide was used to maintain the pH at a setpoint of 7 pH units for each test run. The pH of the influent wastewater was approximately 6.7, based on the previous demonstration, and was monitored during the tests.

Nutrient Addition Rate

The biomass that degrades 2,4-DNT in the WD wastewater utilizes the alcohol and ethers present in the wastewater as sources of energy. In addition, the biomass required supplemental nutrients,

including ammonia and phosphorus, for healthy and sustained growth. Absence of these substances may result in reduced treatment efficiency. A nutrient feed solution was metered into the influent wastewater. The composition of the nutrient mixture is shown in Table 5-3. The rate of nutrient addition was determined by the COD of the influent. A target nutrient to COD ratio was based on the nutrient mixture used in the previous USACERL bench-scale study.

Based on the RBC system vendor's previous experience, it was recommended that a minimum of 0.1 ppm soluble ortho-phosphate should remain in the RBC effluent after treatment. It was assumed that biodegradation of the DAT in the RBC system would provide the necessary nitrogen for biomass growth. Nutrients present in the Envirex effluent were not supplemented in the influent to the RBC. However, on occasion, it was necessary to feed supplemental alcohol to the RBC to maintain the biomass.

Rotation Rate

As discussed earlier, the rotation rate for the RBC unit was approximately 12 rpm. The rotation rate of the RBC was changed as necessary during the demonstration to maintain aerobic conditions in the RBC.

Dissolved Oxygen

The dissolved oxygen content of the Envirex effluent was monitored to ensure greater than 2 mg/L dissolved oxygen was present in the RBC system influent. The wastewater was aerated in the 25 gallon surge/aeration tank to increase dissolved oxygen levels in the RBC influent.

Sampling

The evaluation of the effectiveness of the AnFBR/RBC system focused on the ability of the system to transform DNT to DAT. 2,4-DNT and DAT concentrations were quantified in samples from various points and at various times during the demonstration. Other parameters that were monitored during testing to evaluate the effectiveness of the treatment system included:

Table 5-3. Nutrients and Salts Used During the AnFBR Demonstration

Nutrient	Chemical	Formula	Nutrient	Percent Nutrient of Formula Weight	Grams of Chemical Per 25-Gallon Tank	kg/90 days	Aldrich No.
A1	Ammonium molybdate tetrahydrate	$(NH_4)_6MO_7O_{24}\cdot 4H_2O$	Mo	54.3	2.4	0.029	22,123-6
A2	Sodium borate decahydrate	$Na_2B_4O_7\cdot 10H_2O$	B	11.4	3.6	0.043	22,133-3
A3	Nickel chloride hexahydrate	$NiCl_2\cdot 6H_2O$	Ni	24.7	4.3	0.052	36,430-4
A4	Manganese chloride tetrahydrate	$MnCl_2\cdot 4H_2O$	Mn	27.8	3.7	0.044	22,127-9
A5	Zinc chloride	$ZnCl_2$	Zn	48.0	2.4	0.028	20,808-6
A6	Copper chloride dihydrate	$CuCl_2\cdot 2H_2O$	Cu	37.3	3.0	0.036	30,748-3
A7	Cobalt chloride hexaydrate	$CoCl_2\cdot 6H_2O$	Co	24.8	35	0.415	20,218-5
B1	Bio treatment nutients No. 36		N/P		4090	40.31	MERCK
C1	Magnesium chloride hexaydrate	$MgCl_2\cdot 6H_2O$	Mg	12.0	2770	33.2	10-5480
C2	Calcium chloride	$CaCL_2$	Ca	36.1	940	11.3	10-1630
C3	Potassium chloride	KCl	K	52.4	1860	22.3	10-7495
							ALDRICH
D1	Iron (II) chloride tetraydrate	$FeCl_2\cdot 4H_2O$	Fe	28.1	190	2.3	22,029-9
E1	Sodium sulfide nonaydrate	$Na_2S\cdot 9H_5O$	S	13.4			40,300-8
E2	Table Sugar	Sucrose					

- Flowrate
- pH
- Oxidation-Reduction Potential (ORP)
- Temperature
- Dissolved Oxygen (DO)
- Volatile Fatty Acids (VFA)
- Total Suspended Solids (TSS)
- Sulfate
- Chemical Oxygen Demand (COD)
- Ethanol
- Diethyl Ether
- Offgas Analysis for methane and carbon dioxide

In addition to the daily reactor performance data gathered for the steady-state periods, EFX also collected liquid phase and GAC samples for three selected steady-state periods. These measurements were intended to permit EFX to calculate the kinetics of DNT reduction in the reactor bed and profile the fate of DNT and DAT in the reactor.

The evaluation of the effectiveness of the RBC system focused on the ability of the system to degrade DAT present in the effluent from the AnFBR system. The parameters that were monitored during testing to evaluate the effectiveness of the RBC system were:

- Flowrate
- pH
- Temperature
- Dissolved Oxygen (DO)
- Chemical Oxygen Demand (COD)
- DNT/DAT
- Total Suspended Solids (TSS)

5.5 Pilot-test Results

The demonstration of the AnFBR/RBC system was conducted between September 12, 1994 and July 26, 1995. Based on the operational conditions of the system, and to facilitate discussion, the demonstration has been segmented into the following phases:

Phase	Dates of Operation		
Startup and Acclimation	September 12, 1994	—	January 30, 1995
Test Run No. 1	January 31, 1995	—	February 16, 1995
First Standby Period	February 17, 1995	—	April 16, 1995
Test Run No. 2	April 17, 1995	—	April 28, 1995
Second Standby Period	April 29, 1995	—	May 29, 1995
Test Run No. 3	May 30, 1995	—	June 7, 1995
Test Run No. 4	June 8, 1995	—	June 15, 1995
Test Run No. 5	June 20, 1995	—	June 29, 1995
Test Run No. 6	July 5, 1995	—	July 14, 1995
Test Run No. 7	July 19, 1995	—	July 21, 1995
Test Run No. 8	July 24, 1995	—	July 26, 1995

The discussion of results presented in the following sections address each of these phases individually.

Startup and Acclimation

Operation of the AnFBR system was initiated on September 12, 1994. Startup activities included inoculating the reactor with anaerobic microbes by adding a combination of biomass coated GAC and suspended biomass cultures to the reactor. The addition of the biomass was completed over a period of three days while the reactor was operated in recycle mode. The biomass coated GAC was obtained from pilot-scale reactors operated by EFX at another location that had been acclimated with a laboratory prepared solution of 2,4-DNT and wastewater obtained from a brewery. The suspended biomass inocula was sludge obtained from the effluent of the same pilot-scale reactors.

Following inoculation, the AnFBR was fed a mixture of ethanol and clean plant water at a flow rate of 0.3 gpm. Based on a reactor bed volume of 0.71 m^3 (the bed volume of the expanded bed), this feed rate provided the reactor with an applied organic loading rate (OLR) of 5 kg-COD/m^3 bed/day.

During the first six weeks of acclimation, several operational problems were encountered. These problems, which included reactor shut-downs and pH excursions, are detailed later in this section. As a result of the reactor malfunctions and the attempted remedies, the biomass in the system was lost and the reactor was reinoculated on November 3, 1995. Over a period of three

days, approximately 8 gallons of biological sludge was added to the reactor each day. This sludge was procured from the primary and secondary anaerobic digestors at a local POTW (Pepper's Ferry Wastewater Treatment Plant). During this acclimation period, the reactor was operated in recycle flow.

The reactor was fed a solution of sucrose dissolved in clean plant water for the first week following reinoculation. During the next two weeks, the reactor was fed a 50:50 mixture, on a COD basis, of ethanol and sugar. This feed was again changed on November 25, 1994 to a mixture of 90% ethanol and 10% sugar on a COD basis. The applied OLR throughout this period following reinoculation was maintained at 5 kg-COD/m^3 bed/day. The objective of this effort was to develop a biomass that was acclimated to ethanol at the stated OLR. The OLR was gradually increased to 7 kg-COD/m^3/day on December 28, 1994, and, then, to 10 kg-COD/m^3/day on January 3, 1995. This OLR was maintained for the remaining of the acclimation period.

Water-dry wastewater containing 2,4-DNT was introduced to the system by diluting it with clean plant water starting on January 18, 1995. The wastewater forward flow rate was maintained at 0.4 gpm. The ethanol/sugar solution feed was continued at a reduced feed rate to maintain the OLR to the system at 10 kg-COD/m^3/day. This acclimation to 2,4-DNT wastewater was continued for approximately two weeks prior to initiation of the first test run.

During the start-up period, the RBC, which received effluent from the AnFBR, was inoculated with biomass harvested from the RAAP BWTP RBCs. There was sufficient alcohol present in the AnFBR effluent for maintenance of a viable biomass on the RBC. The disks in the unit were initially rotated at 8 rpm. This speed was later increased to 12 rpm because the high alcohol level in the AnFBR effluent caused the RBC to become anaerobic. The high alcohol level also led to excessive growth on the disks which, on occasion, required removal.

Test Run No.1
The test runs were designated periods of time when the sampling frequency was intensified to once a day (versus approximately three times per week during acclimation). The first test run

was initiated on January 31, and continued through February 16, 1995. During this time, the wastewater flow rate was maintained at 0.4 gpm providing an empty bed hydraulic residence time of 7.8 hours. Table 5-4 shows the analytical data for this operational period. The average concentration of 2,4-DNT in the influent was 154 mg/L with a maximum concentration of 168 mg/L. The feed rate of the supplemental ethanol/sugar solution was adjusted to maintain an OLR of approximately 10 kg-COD/m^3/day. The supplemental feed solution was changed to ethanol only on February 11. The flow rate of alcohol was adjusted to maintain the OLR at approximately 10 kg-COD/m^3/day.

Under anaerobic biological conditions, 2,4-DNT is converted to 2,4-DAT. Removal of 2,4-DNT by biodegradation can be estimated by the formation of DAT in the reactor. However, both 2,4-DNT and DAT are adsorbed on activated carbon. Therefore, it is difficult, initially, to gauge the rate of biodegradation of 2,4-DNT from concentrations of DAT in the effluent. During this operational period, the reactor successfully removed more than 99 percent of the influent 2,4-DNT (Figure 5-3). However, concentrations of DAT observed in the AnFBR effluent were near the analytical detection limit. Therefore, during this test run either the microbial population had not grown sufficiently to degrade all the influent 2,4-DNT to DAT, adsorption of 2,4-DNT on the GAC was masking DAT production, or 2,4DNT was converted to DAT and all of the DAT was adsorbed on the GAC.

Approximately 40 percent of the influent ethanol passed through the AnFBR system untreated. This indicated that insufficient biomass was present in the reactor to oxidize the full ethanol loading. The concentration of acetate in the AnFBR effluent averaged 732 mg/L, indicating that an acetate metabolizing methanogenic population had not yet established itself. The average COD of the influent was 3,400 mg/L, while the average effluent COD was approximately 1,900 mg/L. The ether, 64 mg/L in the influent, was reduced to an average of 21 mg/L in the effluent. This removal may have been due to adsorption on the GAC.

Neither the Wet Test Gas Meter (WTGM) nor the Infra Red Gas Analyzer (IRGA) were operational during this test run due to equipment malfunctions. Therefore, data regarding methane generation in the AnFBR could not be collected.

Table 5-4
Analytical Data for Test Run No. 1
January 31, 1995 - February 16, 1995

	AnFBR Influent									AnFBR Effluent							RBC Effluent						
Date	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD*, (mg/L)	Organic Loading Rate (OLR) (kg-COD/m3/day)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
01/31/95	159	0.251	144	8.2	64	53	Trace	3,163.37	9.70	0.111	0.43	584	6.4	786	7.8	2,100	<0.1	ND	5	ND	412	7.8	1,388
02/01/95	154	0.244	136	8.5	61	47	<2	3,251.19	9.96	0.11	ND	567	8.3	817	8.0	2,138	<0.1	ND	3.2	ND	420	12.1	1,475
02/02/95	152	0.056	147	9.1	63	52	ND	3,451.83	10.58	0.117	ND	445	9.9	768	6.7	1,888	<0.1	ND	1.9	ND	433	11.3	1,350
02/03/95	151	0.22	138	9.28	71	47	<1	3,341.52	10.24	0.113	ND	464	15	922	8.2	1,950	<0.1	ND	1.7	ND	539	11.8	1,300
02/07/95	168	ND	140	7.9	69	54	<1	2,750.33	8.43	<0.10	ND	263	16	852	7.2	1,375	<0.1	ND	ND	ND	566	17.1	863
02/09/95	162	0.028	132	6.8	57	49	<1	2,557.87	7.84	<0.02	ND	143	19	670	2.1	1,025	<0.02	ND	ND	ND	365	6.6	475
02/10/95	151	0.652	136	12.8	68	48	<2	4,131.06	12.66	0.006	<0.01	675	24	678	<2.0	1,700	<0.01	0.08	32	2.5	451	7.8	1,313
02/13/95	150	0.812	135	11.6	61	56	<2	3,812.02	11.68	<0.006	0.21	672	29	652	<2.0	1,800	<0.01	0.29	17	3.3	306	2.2	1,400
02/14/95	149	0.887	132	11.7	63	55	<2	3,835.61	11.76	0.006	0.41	690	37	648	<2.0	2,125	<0.01	0.38	14	ND	305	2.8	1,375
02/15/95	145	1.006	141	9.27	67	54	<2	3,134.56	9.61	0.008	0.49	739	31	690	<2.0	2,200	0.009	0.49	69	4.5	233	3.5	1,250
02/16/95	148	0.994	140	12.5	61	55	<2	3,978.30	12.19	0.01	0.74	919	38	574	<2.0	2,450	0.008	0.72	35	8.8	284	<2	2,010
Average	154	0.52	138	9.79	64	52	1.67	3400.70	10.42	0.06	0.38	560	21	732	4.5	1886	<0.05	0.39	19.9	4.8	392	7.7	1291
Maximum	168	1.01	147	12.80	71	56	<2.00	4131.06	12.66	0.117	0.74	919	38	922	8.2	2450	<0.10	0.72	69.0	8.8	566	17.1	2010

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

Figure 5-3

DNT Removal and DAT Appearance During Test Run No. 1

January 31, 1995 - February 16, 1995

Wastewater Flow Rate = 0.4 gpm

Organic Loading Rate = 10 kg-COD/m³/day

Retention Time = 7.8 hours
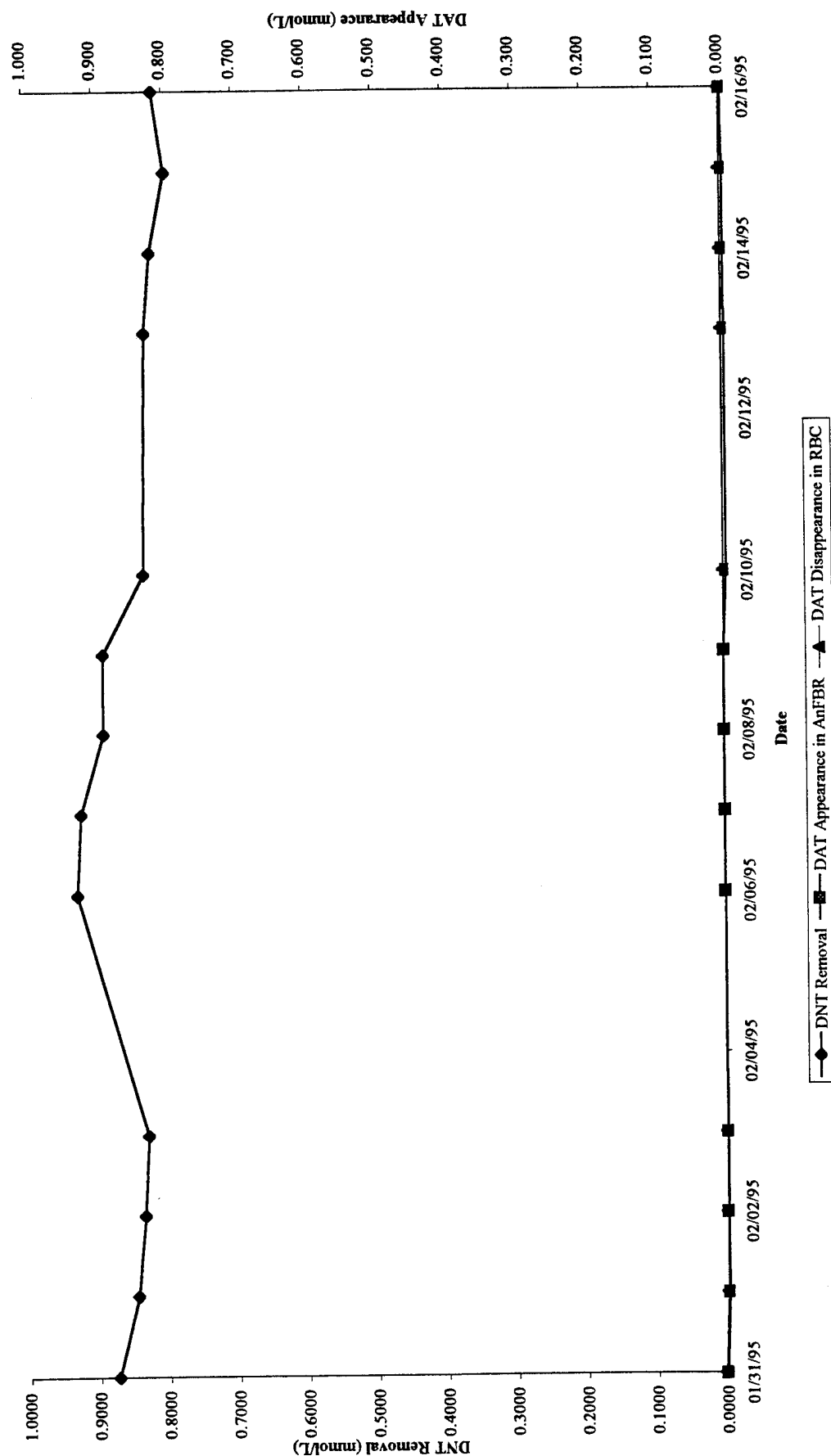
The RBC degraded 96 percent of the alcohol contained in the AnFBR effluent. However, only 56 percent of the acetate was degraded by the RBC indicating that an adequate microbial population had not yet been established to metabolize the acetate. The RBC effluent had a COD of approximately 1,300 mg/L.

First Standby Period
Following completion of the first test run, the initial supply of water-dry wastewater was exhausted. Because production of single base propellants had been interrupted due to changes in the production schedules, WD wastewater containing 2,4-DNT was not available again until March 28, 1995. In an effort to keep the biomass active and viable until WD wastewater was available, the reactor was switched to a forward feed of plant water at 0.4 gpm and the supplemental ethanol feed was resumed. The ethanol feed rate was adjusted to maintain an OLR of 10 kg-COD/m^3/day. However, problems were encountered with the alcohol feed pump that caused this flow rate to fluctuate significantly during the standby period. This problem was eliminated through the installation of a new pump prior to the start of the second test run. The WTGM and IRGA were repaired during this period. Operational data collected during this period are summarized in Table 5-5.

During this standby period, gas production from the reactor ceased unexpectedly indicating a cessation of biological respiration. A review of operating conditions did not reveal any apparent problems that could have caused this situation. Researchers involved in the previous bench-scale evaluation of AnFBR for USACERL suggested that a deficiency in sulfide could be a potential cause. In an attempt to revive microbial activity, sodium sulfide ($Na_2S\cdot9H_2O$) was added to the supplemental alcohol feed solution in a quantity sufficient to provide 2 mg/L sulfide (S) at 0.4 gpm influent water feed. Addition of the supplemental sulfide was started on April 7, 1995, and gas production resumed on April 13, 1995. It is not known whether the sulfide addition solved the problem or whether some unidentified transient condition existed.

Test Run No. 2
Upon collection of the next available batch of WD wastewater, the second test run was initiated on April 17 and continued through April 28, 1995. The wastewater flow rate was maintained at

Table 5-5
Analytical Data for First Standby Period
February 17, 1995 – April 16 1995

	AnFBR Influent									AnFBR Effluent							RBC Effluent						
Date	DNT (mg/L)	DAT (mg/L)	Alcohol (mg/L)	Alcohol Feed (mL/min)	Ether (mg/L)	Acetic Acid (mg/L)	Propionic Acid (mg/L)	Calculated COD* (mg/L)	Organic Loading Rate (kg-COD/m3/day)	DNT (mg/L)	DAT (mg/L)	Alcohol (mg/L)	Ether (mg/L)	Acetic Acid (mg/L)	Propionic Acid (mg/L)	COD (mg/L)	DNT (mg/L)	DAT (mg/L)	Alcohol (mg/L)	Ether (mg/L)	Acetic Acid (mg/L)	Propionic Acid (mg/L)	COD (mg/L)
02/17/95	NA	NA	NA	12.5	NA	NA	NA	3,323.30	10.19			NA	NA	NA	NA				NA	NA	NA	NA	
02/21/95	NA	NA	NA	3.3	NA	NA	NA	877.35	2.69			NA	NA	NA	NA				NA	NA	NA	NA	
2/22/95	0	0	0	12.8	0	0	0	3,403.06	10.43	NA	NA	NA	NA	NA	NA	483	NA	NA	NA	NA	NA	NA	66
2/23/95	0	0	0	12.1	0	0	0	3,220.05	9.87	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2/24/95	0	0	0	1.3	0	0	0	345.62	1.06	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2/27/95	0	0	0	1.1	0	0	0	292.45	0.90	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2/28/95	0	0	0	0.7	0	0	0	186.10	0.57	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	62
3/01/95	0	0	0	4.6	0	0	0	1,222.97	3.75	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
3/02/95	0	0	49	3.2	21.8	385	<2	1,377.76	4.22	NA	NA	21.6	22.1	404	<2	476	NA	NA	ND	ND	1.9	ND	62
3/03/95	0	0	0	3.3	0	0	0	877.35	2.69	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
3/06/95	0	0	0	8.4	0	0	0	2,233.26	6.84	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
03/07/95	0	0	635	7.9	21.2	198	ND	3,555.33	10.90	0	0	624	21.2	202	ND	1,480	0	0	145	1.3	78	14	947
03/09/95	0	0	601	8.1	19.9	316	ND	3,738.50	11.46	0	0	597	20.2	325	ND	1,590	0	0	122	18.9	124	6.2	1,145
03/14/95	0	0	596	13.2	18	350	<2.0	3,386.70	10.38	0	0	602	20	369	<2.0	1,622	0	0	38	3.5	194	8.6	979
03/15/95	0	0	NA	11.6	NA	NA	NA	3,084.02	9.45	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
03/16/95	0	0	654	13.3	21	387	<2.0	3,574.00	10.95	0	0	686	18	393	<2.0	1,824	0	0	154	3.8	191	<2	1,279
03/17/95	0	0	0	10.3	NA	NA	NA	1,369.20	4.20	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
03/20/95	0	0	NA	10.4	NA	NA	NA	1,382.49	4.24	0	0	NA	NA	NA	NA	1,164	0	0	NA	NA	NA	NA	713
03/21/95	0	0	432	12.7	20.1	319	<2.0	2,854.24	8.75			440	19.6	325	<2.0				119	ND	139	3.1	
03/22/95	0	0	NA	10.2	NA	NA	NA	1,355.91	4.16	0	0	NA	NA	NA	NA	1,470	0	0	NA	NA	NA	NA	894
03/23/95	0	0	587	11.2	21.4	374	ND	2,982.84	9.14			577	23.3	387	ND				10.9	ND	152	3.6	
03/24/95	0	0	NA	9.7	NA	NA	NA	2,578.88	7.90	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
03/27/95			NA	10.5	NA	NA	NA	1,656.02	5.08			NA	NA	NA	NA				NA	NA	NA	NA	
03/28/95	251.50	<0.10	205	6.4	83	17.9	ND	1,009.38	3.09	<0.05	<0.10	132	17	497	<2.0	786	<0.05	0.28	ND	ND	87	<2	188
03/30/95	239.00	0.1	245	7.4	105	11.8	<2	1,577.55	4.83			NA	NA	NA	NA				NA	NA	NA	NA	
03/31/95	148.00	<0.50	257	9.2	114	23.0	<2	7,197.62	22.06	<0.01	1.89	ND	35	577	8.3	745	<0.01	<0.01	ND	ND	10.9	ND	78
04/04/95	199.00	<0.50	250	6.53	118	22.0	0	1,614.94	4.95	<0.01	3.03	ND	44	575	6.1	745	<0.01	2.63	ND	ND	10.4	ND	89
04/06/95			NA	7.2	NA	NA	NA	1,802.78	5.53			NA	NA	NA	NA				NA	NA	NA	NA	
04/07/95	213.75	<0.10	253	4.76	119	18.4	ND	3,143.99	9.64	<0.05	8.59	26	85	793	<2.0	949	<0.05	7.76	ND	ND	55	ND	
04/12/95	NA	NA	NA	9.0	NA	NA	NA	1,707.01	5.23	<0.05		NA	NA	NA	NA		<0.05		ND	ND	NA	NA	234
04/13/95	NA	NA	NA	14.6	NA	NA	NA	9,643.33	29.55			NA	NA	NA	NA				NA	NA	NA	NA	

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

0.4 gpm again providing an empty bed hydraulic residence time of 7.8 hours. Table 5-6 presents a summary of the analytical data collected during this operational period. The average concentration of 2,4-DNT in the untreated wastewater was 181 mg/L with a maximum concentration of 213 mg/L. The feed rate of the supplemental ethanol was adjusted to maintain an approximate OLR of 5 kg-COD/m^3/day.

During this period, the reactor successfully reduced the influent concentration of 2,4-DNT to non-detectable levels in the AnFBR effluent. The concentration of DAT in the effluent averaged 22 mg/L with a maximum concentration of 29 mg/L. Figure 5-4 presents a graph, on a molar basis, (mmol/L) showing removal of 2,4-DNT from the influent, and the appearance of DAT in the effluent. As can be seen from this graph, the formation of DAT approaches the disappearance of 2,4-DNT, indicating conversion of the 2,4-DNT to DAT.

Approximately 97 percent of the alcohol in the influent was reduced by the system indicating the presence of an adequate biomass in the reactor to accomplish ethanol oxidation. The concentration of acetate in the effluent averaged 529 mg/L, indicating that an acetate metabolizing methanogenic population had not yet been established. The average COD of the influent was approximately 1,700 mg/L; the average COD in the effluent was approximately 850 mg/L. The ether present in the influent (≈120 mg/L) passed through the system without change indicating that it was not being biodegraded or absorbed.

The WTGM recorded gas flow rates up to 16.5 L/hr during this period. The concentration of methane in the reactor offgas, as measured by the IRGA, ranged between 70 and 85 percent. Carbon dioxide was not detected in the off gas.

DAT removal in the RBC was approximately 26 percent. However, all of the alcohol and ether, and approximately 90 percent of the acetate present in the AnFBR effluent were degraded by the RBC. The COD in the RBC effluent was approximately 177 mg/L (versus an influent COD of 848 mg.L).

Table 5-6
Analytical Data for Test Run No. 2
April 17, 1995 - April 28, 1995

	AnFBR Influent										AnFBR Effluent							RBC Effluent						
Date	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD *, (mg/L)	Organic Loading Rate (kg-COD/m³/day)		DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
04/17/95	169.60	0.342	251	8.65	126	20	<2	1,621.04	4.97		<0.05	14.198	ND	113	488	<2	707	<0.05	10.566	ND	0.2	ND	ND	166
04/18/95	173.70	0.306	251	0	126	19	ND	1,126.00	3.45		<0.05	15.598	ND	115	304	<2	557	<0.05	3.179	ND	ND	ND	ND	101
04/19/95	199.00	0.283	247	6.57	109	18	ND	1,532.46	4.70		<0.05	16.958	ND	112	584	2.0	823	<0.05	12.079	ND	ND	2.5	ND	114
04/20/95	209.40	<0.1	246	11.3	124	26	ND	1,834.41	5.62		<0.05	18.435	15	114	676	<2	911	<0.05	17.189	ND	0.2	10.8	ND	162
04/21/95	159.50	0.326	254	8.0	126	25	ND	1,616.24	4.95		<0.05	22.06	ND	122	557	6.3	842	<0.05	18.47	ND	0.8	4.9	ND	165
04/24/95	144.58	0.504	248	10.0	119	24	<2	1,695.79	5.20		<0.05	25.04	ND	124	259	2.0	576	<0.05	3.53	ND	ND	3	ND	60
04/25/95	198.30	0.5	249	11.9	116	22	0	1,836.07	5.63		<0.05	26.89	20	130	567	<2.0	962	<0.05	25.13	ND	2	132	ND	293
04/26/95	176.3	<0.10	247	13.7	117	24	0	1,899.08	5.82		<0.05	26.71	45	124	624	<2.0	1,023	<0.05	25.40	ND	6	137	ND	315
04/27/95	213.00	0.453	248	13	121	24	0	1,906.13	5.84		<0.05	28.93	47	132	620	<2.0	1,047	<0.05	25.38	ND	6	75	ND	228
04/28/95	168.01	0.54	248	12.3	121	25	0	1,814.19	5.56		<0.05	27.70	36	131	611	2.0	1,028	<0.05	25.73	ND	2	22	ND	168
Average	181.14	0.35	249	9.54	121	23	<0.67	1688.14	5.17		<0.05	22.25	33	122	529	2.43	848	<0.05	16.67	ND	2	48	ND	177
Maximum	213.00	0.54	254	13.70	126	26	<2.00	1906.13	5.84		<0.05	28.93	47	132	676	6.30	1047	<0.05	25.73	ND	6	137	0.00	315

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

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Figure 5-4
DNT Removal and DAT Appearance During
Test Run No. 2
April 17, 1995 - April 28, 1995

Wastewater Flow Rate = 0.4 gpm
Organic Loading Rate = 5 kg-COD/m³/day
Retention Time = 7.8 hours
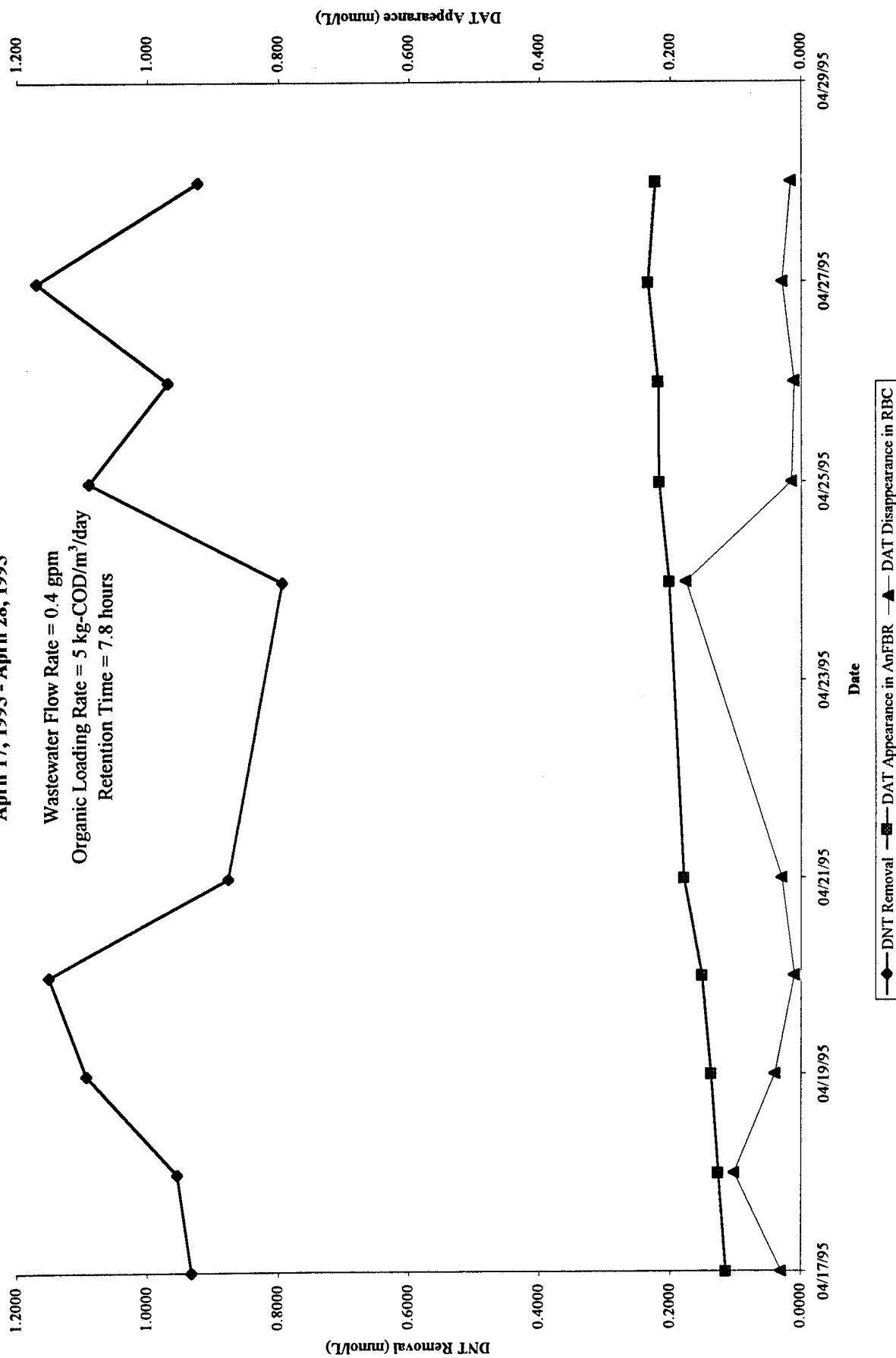
Second Standby Period

Following completion of the second test run, the supplemental alcohol feed was gradually reduced until the feed was stopped entirely on May 8, 1995. The objective of this change was to determine if the alcohol present in the WD wastewater was sufficient to maintain the biomass in the AnFBR. The nutrient and sodium sulfide solutions were maintained at the same rates as the previous run. WD wastewater was fed to the system at a forward flow rate of 0.4 gpm. Table 5-7 presents the analytical results from the second standby period. The system continued to degrade alcohol and 2,4-DNT and the concentration of DAT in the effluent continued to increase. A graphical comparison of the concentration of 2,4-DNT in the influent and the concentrations of DAT in the effluent, on a molar basis, is presented in Figure 5-5. The graph shows good correlation of the molar conversion of 2,4-DNT to DAT. During this period, the system continued to produce approximately 5 L/hr of gas.

The RBC achieved a low rate of removal of DAT (26 percent) during the second standby period. The AnFBR effluent (i.e., the influent to the RBC) contained a low concentration of ethanol. To stimulate microbial growth in the RBC, a small amount (approximately 3 mL/min) of supplemental alcohol was fed to the RBC during the second standby period. The addition of alcohol to the RBC appeared to boost the microbial population sufficiently to enable it to reduce DAT to levels below detection. The biomass in the RBC also degraded influent alcohol, ether, and acetate which were not detected in the RBC effluent.

Table 5-7
Analytical Data for Second Standby Period
April 29, 1995 - May 29, 1995

Date	AnFBR Influent DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD*, (mg/L)	Organic Loading Rate (kg-COD/m³/day)	AnFBR Effluent DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	RBC Effluent DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
04/29/95			NA	12.6	NA	NA	NA	791.02	2.42	<0.05		NA	NA	NA	NA		<0.05		NA	NA	NA	NA	
05/01/95	204.65	3.3	239	12.2	116	33.0	0	1,859.91	5.70	<0.05	35.31	ND	132	563	2.0	919	<0.05	31.18	ND	2	44	ND	229
05/02/95	205.68	1.11	234	11.5	111	26.0	0	1,748.96	5.36	<0.05	35.13	ND	134	618	3.0	979	<0.05	28.44	ND	2	5	ND	189
05/03/95	183.72		NA	6.86	NA	NA	NA	430.67	1.32			NA	NA	NA	NA				NA	NA	NA	NA	
05/04/95	189.27	0.76	208	6.3	77	22	0	1,366.51	4.19	<0.05	39.56	ND	102	563	2	921	<0.05	31.37	ND	<2	4	ND	159
05/09/95	194.80	<0.05	211	4.85	74	26.0	<2	1,034.00	3.17	<0.05	47.76	ND	91	206	4.0	580	<0.05	0.96	ND	ND	3	ND	138
05/11/95	181.92	0.383	221	3.5	78	22.0	ND	1,025.00	3.14	<0.05	51.10	ND	92	175	4.0	545	<0.05	<0.05	ND	ND	<2	ND	108
05/16/95	154.60	0.732	179	10.6	58	20.0	ND	848.00	2.60	<0.05	61.55	ND	87	107	<2.0	499	<0.05	0.69	ND	ND	<2	ND	140
05/18/95	152.38	0.376	170	11.9	67	25.0	<2	822.00	2.52	0.157	62.06	ND	82	117	3.0	517	<0.05	0.69	ND	ND	<2	ND	184
05/22/95	147.71	0.515	161	11.2	63	27.0	<2	822.00	2.52	<0.05	73.61	ND	74	81	3.0	456	<0.05	9.62	ND	ND	<2	ND	184
05/23/95	145.50	0.647	164	10.9	62	25.0	ND	813.00	2.49	<0.05	76.80	ND	73	74	3.0	427	<0.05	<0.10	ND	ND	<2	ND	72
05/25/95	142.41	0.474	164	12.2	64	26.0	<2	823.00	2.52	<0.05	80.16	ND	76	66	<2.0	417	<0.05	<0.10	ND	ND	<2	ND	72

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

Figure 5-5
DNT Removal and DAT Appearance During
Standby Period No. 2
April 29, 1995 - May 29, 1995

Wastewater Flow Rate = 0.4 gpm
Organic Loading Rate = 2.5 kg-COD/m³/day
Retention Time = 7.8 hours
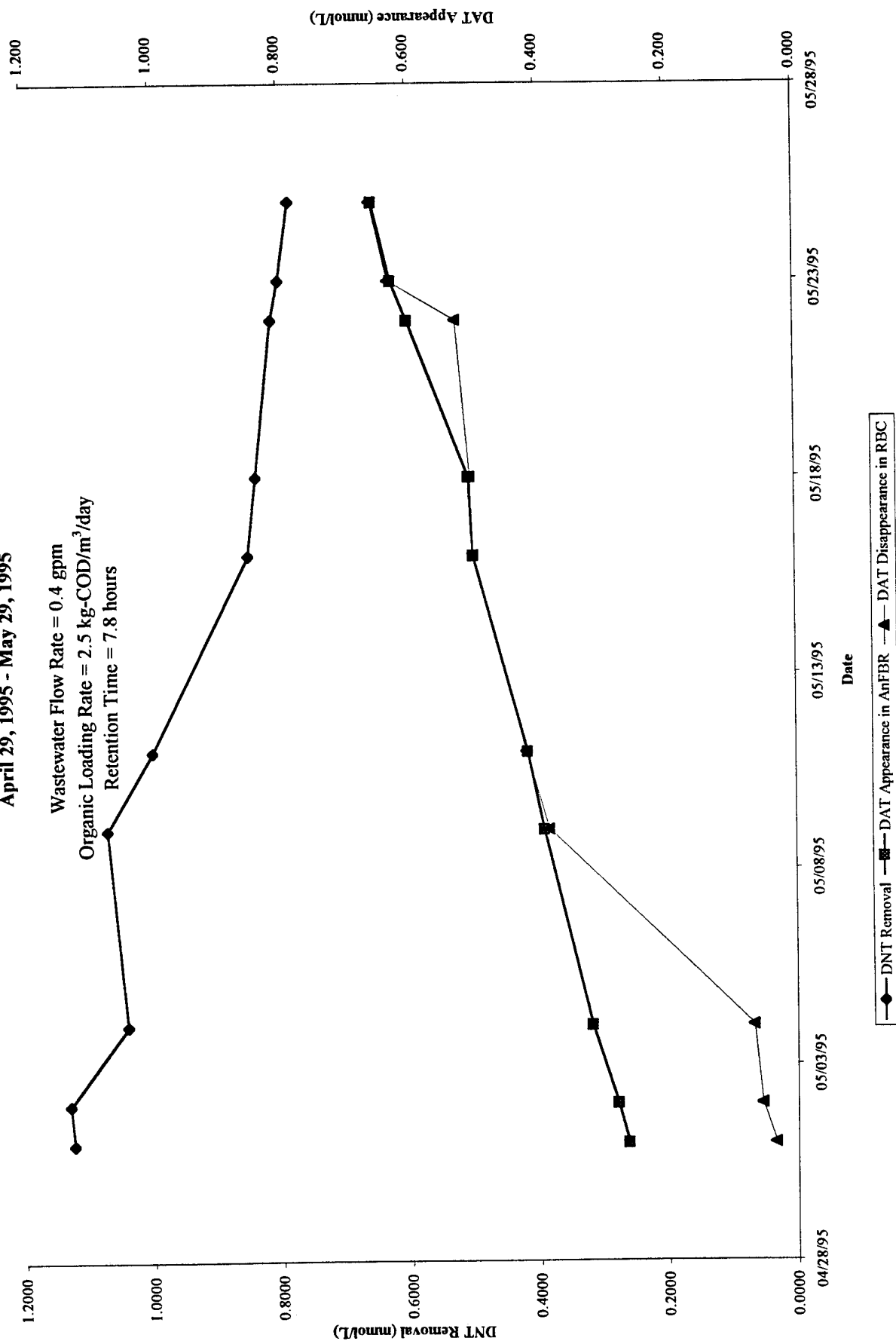
Test Run No. 3

The third test run was conducted between May 30 and June 7, 1995 (Table 5-8). The forward flow of WD wastewater was maintained at 0.4 gpm providing an empty bed hydraulic residence time of 7.8 hours. Supplemental alcohol was not fed to the system. The average concentration of 2,4-DNT in the untreated wastewater was 164 mg/L with a maximum concentration of 180 mg/L. The approximate OLR to the system was calculated to be 2.5 kg-COD/m^3/day. Since no supplemental alcohol was added, this OLR represents the organic content of the WD wastewater alone.

During this operational period, the reactor successfully reduced 2,4-DNT to levels below detection. The concentration of DAT in the effluent averaged 91 mg/L with a maximum concentration of 95 mg/L. The removal of 2,4-DNT and the appearance of DAT in the effluent during this run is shown in Figure 5-6. On a molar basis, the formation of DAT approached the amount of 2,4-DNT removed. This indicates bio-conversion of 2,4-DNT to DAT on an equimolar basis. The equimolar bio-conversion of 2,4-DNT to DAT in previous runs may have been masked by adsorption of the two compounds on the activated carbon.

Alcohol in the influent was reduced by the AnFBR system to non-detectable levels. The acetate concentration in the effluent averaged 26 mg/L, indicating significant growth of an acetate metabolizing methanogenic biomass. The average COD was 800 mg/L in the influent and approximately 390 mg/L in the effluent. Ether passed through the system without reduction indicating that biodegradation of ether was not occurring.

The AnFBR produced gas flow rates up to 9 L/hr during this period. The methane concentration in the reactor offgas, as measured by the IRGA, averaged 77 percent. Carbon dioxide was not detected in the reactor off gas.

The RBC continued to perform well and degraded the DAT present in the effluent of the AnFBR to levels below detection. Alcohol, ether, and acetate present in the AnFBR effluent were also degraded completely by the RBC. The COD of the RBC effluent was approximately 77 mg/L (influent COD was approximately 390 mg/L).

Table 5-8
Analytical Data for Test Run No. 3
May 30, 1995 - June 7, 1995

	AnFBR Influent									AnFBR Effluent							RBC Effluent						
Date	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD*, (mg/L)	Organic Loading Rate $(\text{kg-COD/m}^3\text{/day})$	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
05/30/95	141.00	<0.10	156	0	56	32	2	805.00	2.47	<0.05	83.98	ND	65	41	ND	379	0.058	<0.10	ND	ND	3	ND	94
05/31/95	142.00	<0.10	162	0	59	32	ND	806.00	2.47	<0.05	86.64	ND	67	37	ND	418	<0.05	<0.10	ND	ND	<2	ND	90
06/01/95	158.46	<0.10	150	0	58	33	ND	803.00	2.46	<0.05	89.56	ND	63	40	ND	414	<0.05	<0.10	ND	ND	<2	ND	71
06/02/95	175.70	<0.10	146	0	61	32	ND	794.00	2.43	<0.05	89.58	ND	65	31	ND	380	<0.05	0.63	ND	ND	2	ND	69
06/04/95	172.20	<0.10	152	0	60	30	<2	774.00	2.37	<0.05	94.65	ND	64	21	ND	367	<0.05	<0.10	ND	ND	<2	ND	60
06/05/95	171.00	<0.10	152	0	61	28	ND	768.00	2.35	<0.05	94.84	ND	67	18	ND	394	<0.05	<0.10	ND	ND	<2	ND	55
06/06/95	174.00	<0.10	148	0	58	25	ND	788.00	2.42	<0.05	94.76	ND	61	14	ND	369	0.048	<0.10	ND	ND	<2	ND	97
06/07/95	180.00	<0.10	129	0	60	27	ND	770.00	2.36	0.097	95.20	ND	60	7	ND	394							77
Average	164.30	<0.10	149	0.00	59	30	<2.00	788.50	2.42	<0.06	91.15	ND	64	26	ND	389	<0.05	0.17	ND	ND	2	ND	77
Maximum	180.00	<0.10	162	0.00	61	33	<2.00	806.00	2.47	<0.10	95.20	ND	67	41	ND	418	<0.06	0.63	ND	ND	3	ND	97

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

Figure 5-6
DNT Removal and DAT Appearance During Test Run No. 3
May 30, 1995 - June 7, 1995

Wastewater Flow Rate = 0.4 gpm
Organic Loading Rate = 2.5 kg-COD/m^3/day
Retention Time = 7.8 hours

DNT Removal — DAT Appearance in AnFBR — DAT Disappearance in RBC
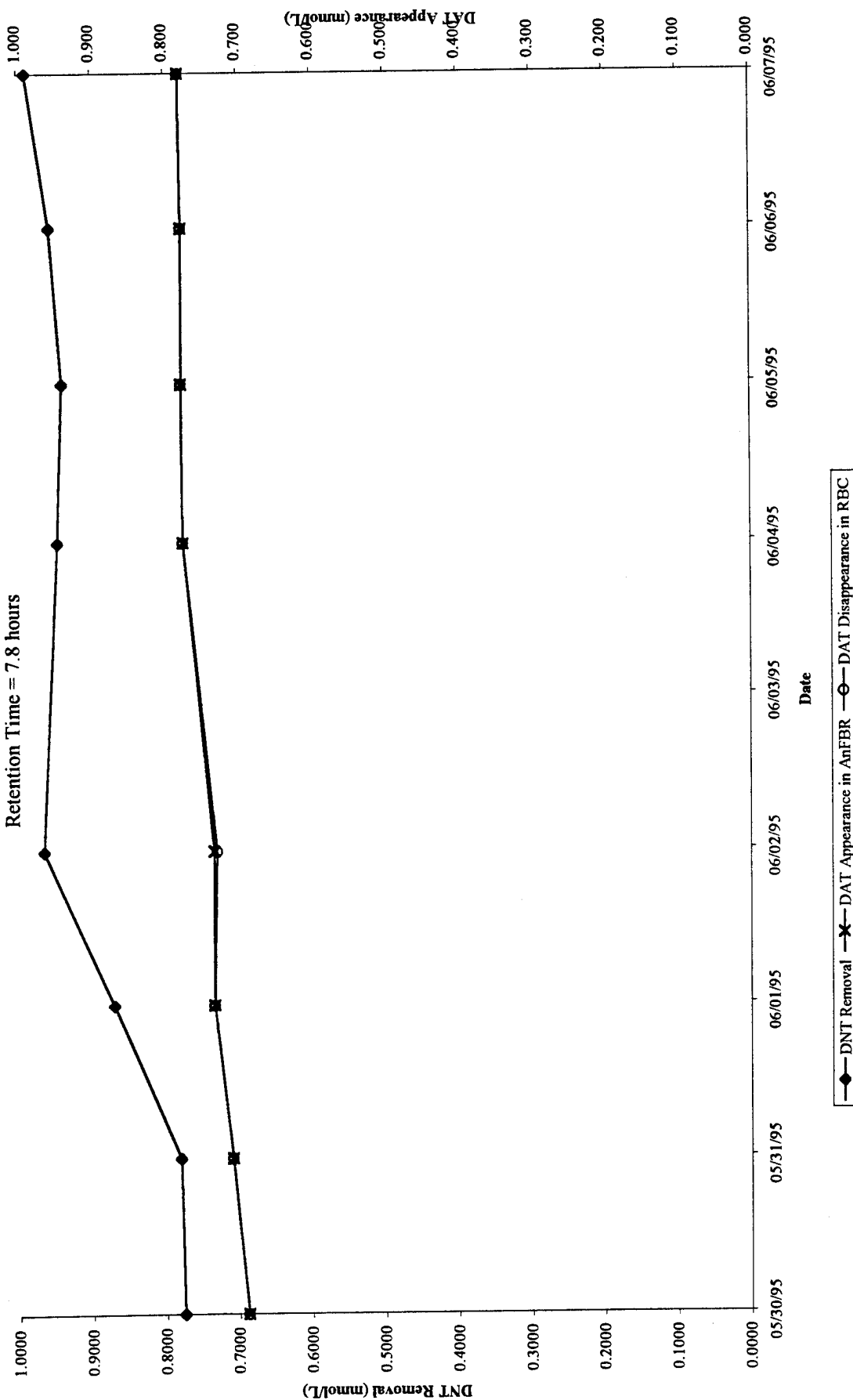
Test Run No. 4

Between June 8 and 15, 1995 data was collected during the fourth test run (Table 5-9). The influent wastewater flow rate was doubled to 0.8 gpm. This rate provided an empty bed hydraulic residence time of 3.9 hours. Again, supplemental alcohol was not fed to the system. The average concentration of 2,4-DNT in the untreated WD wastewater was 189 mg/L with a maximum concentration of 199 mg/L. Under these conditions, the approximate OLR to the system was 4.3 kg-COD/m^3/day which represented the organic content of the WD wastewater alone.

During this operational period, the AnFBR reactor reduced 2,4-DNT to an average concentration of 0.22 mg/L. The maximum concentration of 2,4-DNT in the AnFBR effluent was 0.6 mg/L. DAT in the AnFBR effluent averaged 109 mg/L with a maximum concentration of 129 mg/L. The removal of 2,4-DNT and appearance of DAT in the AnFBR effluent are shown in Figure 5-7. The concentrations of both compounds are plotted on a molar basis. As was observed during the previous test, the amount of DAT in the effluent indicated almost complete bio-conversion of 2,4-DNT to DAT.

Alcohol was reduced to levels below detection in the effluent. Acetate averaged 11 mg/L in the effluent, indicating significant growth of an acetate metabolizing methanogenic culture. The COD was reduced from 700 to approximately 400 mg/L. Ether (approximately 63 mg/L) again passed through the system without reduction (i.e., it was neither adsorbed on the carbon nor biodegraded by the microbes present).

During this period the AnFBR produced a gas flow rate of up to 9 L/hr. The methane concentration in the offgas averaged 73 percent, carbon dioxide was not detected.

The RBC reduced the 2,4-DNT present in the AnFBR effluent (0.22 mg/L average) to an average concentration of 0.11 mg/L. The maximum concentration of 2,4-DNT in the RBC effluent was 0.185 mg/L. During this period, the RBC reduced DAT concentrations by approximately 40 percent, whereas all of the alcohol, ether, and acetate present in the AnFBR effluent were removed. The COD of the RBC effluent averaged 175 mg/L versus influent concentrations of 400 mg/L.

Table 5-9
Analytical Data for Test Run No. 4
June 8, 1995 - June 15, 1995

	AnFBR Influent									AnFBR Effluent							RBC Effluent						
Date	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD*, (mg/L)	Organic Loading Rate (kg-COD/m³/day)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
06/08/95	182	<0.10	138	0	65	31	ND	786	4.82	0.064	90.20	ND	66	34	ND	396	0.087	48.16	ND	ND	3	ND	148
06/09/95	187	0.534	114	0	64	31	ND	744	4.56	0.11	99.98	ND	65	16	ND	385	0.16	49.13	ND	ND	3	ND	140
06/12/95	190	<0.10	68	0	62	39	ND	686	4.20	0.198	110.97	ND	66	<2.0	ND	394	0.185	53.20	ND	ND	<2	ND	162
06/13/95	199	0.549	69	0	62	33	ND	678	4.16	0.119	115.01	ND	66	<2.0	ND	415	<0.05	56.03	ND	ND	<2	ND	167
06/15/95	189	<0.10	66	0	63	28	ND	629	3.86	0.6	129.50	ND	66	<2.0	ND	410	<0.05	98.74	ND	ND	<2	ND	259
Average	189	<0.28	91	0	63	32	ND	705	4.32	0.22	109.13	ND	66	11	ND	400	0.11	61.05	ND	ND	2	ND	175
Maximum	199	0.55	138	0	65	39	ND	786	4.82	0.60	129.50	ND	66	34	ND	415	0.185	98.74	ND	ND	3	ND	259

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

6/5/96

Figure 5-7
DNT Removal and DAT Appearance During Test Run No. 4
June 8, 1995 - June 15, 1995

Wastewater Flow Rate = 0.8 gpm
Organic Loading Rate = 4.3 kg-COD/m^3/day
Retention Time = 3.9 hours
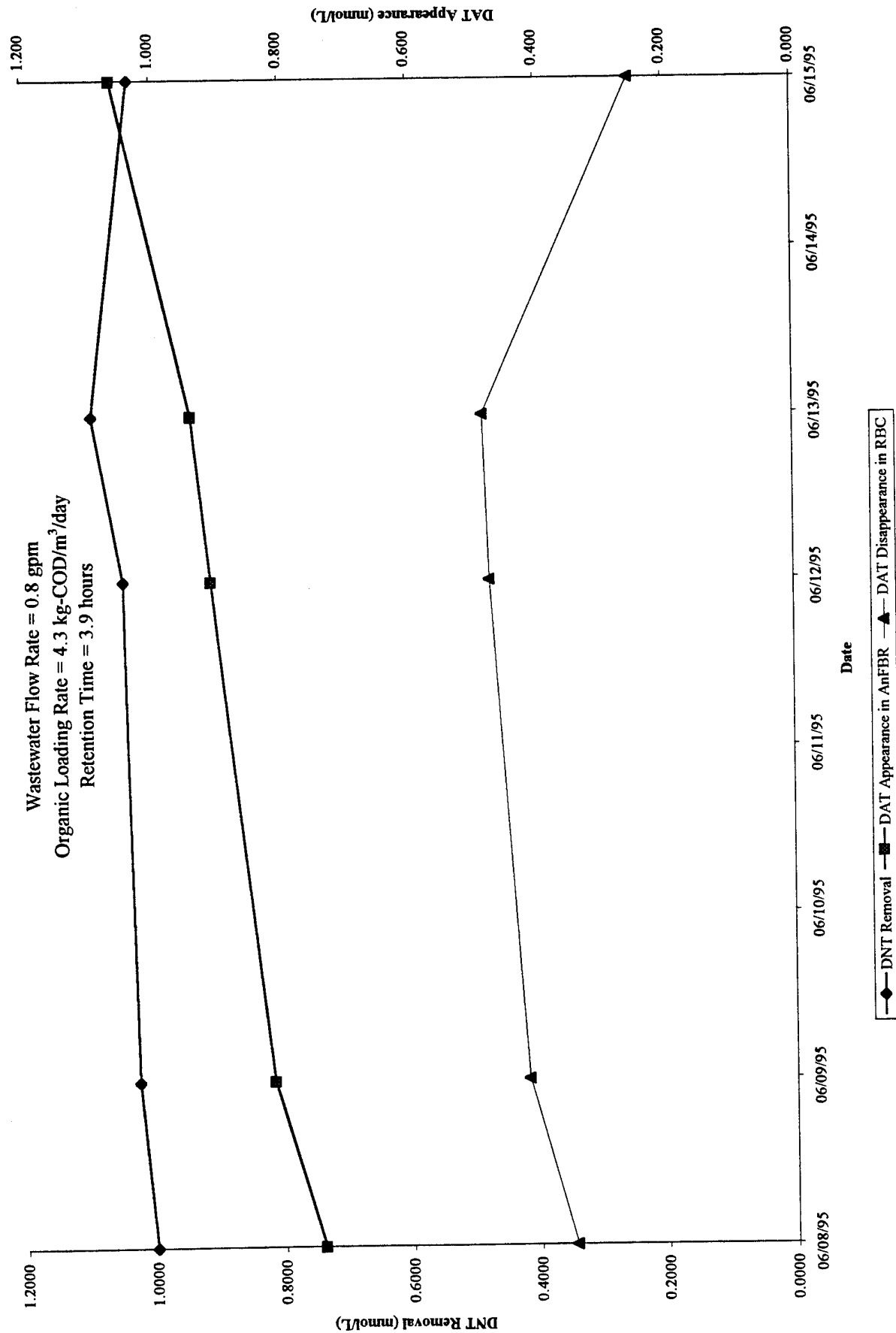
Test Run No. 5

The fifth test run was conducted between June 20 and June 29, 1995 (Table 5-10). Wastewater flow rate was maintained at 0.8 gpm providing an empty bed hydraulic residence time of 3.9 hours. However, supplemental alcohol was fed to the system at a rate of 243 mg/L. The approximate OLR was 6.4 kg-COD/m^3/day. The concentration of 2,4-DNT was reduced from an average of 115 mg/L (maximum concentration 130 mg/L) to an average of 0.07 mg/L (maximum concentration 0.13 mg/L). The concentration of DAT in the effluent averaged 116 mg/L with a maximum concentration of 126 mg/L. The performance of the AnFBR system in removing 2,4-DNT is shown in Figure 5-8. This figure also shows DAT concentrations in the effluent. The concentrations of both compounds are plotted on a molar basis. The concentration of DAT in the effluent exceeded the concentration of 2,4-DNT in the influent. This suggested that both biological conversion of 2,4-DNT to DAT and desorption of DAT from the GAC were occurring in the AnFBR reactor.

Alcohol was reduced to levels below detection in the AnFBR effluent. Acetate concentrations in the effluent averaged 21 mg/L. The COD was reduced from an average of 1,000 mg/L to approximately 400 mg/L. Ether again passed through the system without reduction.

Gas flow rates of up to 31 L/hr were measured during this period. The methane concentration in the reactor offgas averaged 87 percent. Carbon dioxide was not detected.

Concentrations of 2,4-DNT were below detection (<0.10 mg/L) in three of the four samples. In the fourth sample, 0.13 mg/L 2,4-DNT was present. Concentrations of 2,4-DNT in the RBC effluent were below 0.10 mg/L in two of the samples and 0.17 mg/L in the last two samples. The RBC degraded 26 percent of the influent DAT, whereas it degraded all the alcohol, ether, and acetate in the AnFBR effluent. The COD in the RBC effluent was approximately 280 mg/L.

Table 5-10
Analytical Data for Test Run No. 5
June 20, 1995 - June 29, 1995

	AnFBR Influent									AnFBR Effluent							RBC Effluent						
Date	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD*, (mg/L)	Organic Loading Rate (kg-COD/m³/day)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
06/20/95	127.50	<0.10	52	15.3	69	14	ND	1,144.78	7.02	<0.10	126.42	ND	63	27	16	455	0.07	117.60	ND	<2	<2	ND	296
06/22/95	129.67	<0.10	51	15	69	17	ND	1,153.32	7.07	<0.10	119.17	ND	63	36	43	512	<0.10	108.00	ND	<2	<2	ND	287
06/27/95	127.30	<0.10	49	13.17	64	20	3	1,050.27	6.44	<0.10	112.58	ND	63	17	38	449	0.165	68.21	ND	ND	<2	ND	197
06/29/95	75.41	<0.10	34	10.3	43	10	3	836.01	5.12	0.13	108.35	ND	58	5	19	162	0.17	50.14	ND	ND	<2	ND	336
Average	114.97	<0.10	47	13.44	61	15	1.2	1046.10	6.41	0.11	116.63	ND	62	21	29	395	0.13	85.99	ND	ND	2	ND	279
Maximum	129.67	<0.10	52	15.30	69	20	3.0	1153.32	7.07	0.13	126.42	ND	63	36	43	512	0.170	117.60	ND	ND	2	ND	336

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

Figure 5-8
DNT Removal and DAT Appearance During Test Run No. 5
June 20, 1995 - June 29, 1995

Wastewater Flow Rate = 0.8 gpm
Organic Loading Rate = 6.4 kg-COD/m³/day
Retention Time = 3.9 hours

DNT Removal — DAT Appearance in AnFBR — DAT Appearance in RBC — DAT Disappearance in RBC
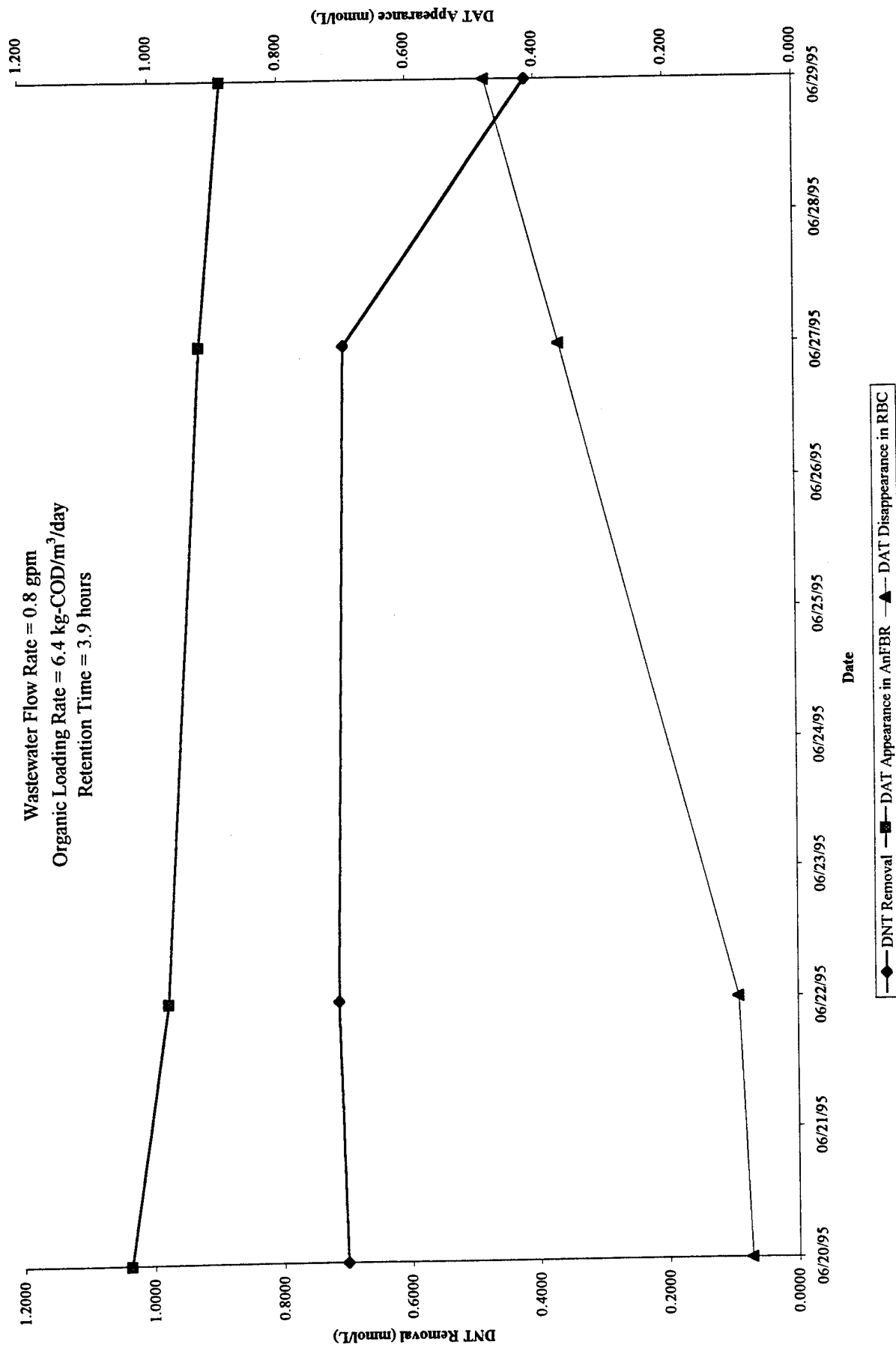
Test Run No. 6

Between July 5 and July 14, 1995, the flow of WD wastewater was maintained at a flow rate of 0.8 gpm through the AnFBR providing an empty bed hydraulic residence time of 3.9 hours. Supplemental alcohol feed to the system continued at the same rate as the previous run. Table 5-11 presents the analytical data for this operational period. The average concentration of 2,4-DNT in the feed wastewater was 62 mg/L with a maximum concentration of 72 mg/L. The approximate OLR to the system was 5 kg-COD/m^3/day.

During this operational period, the reactor reduced the influent 2,4-DNT to non-detectable levels. The DAT concentration in theAnFBR effluent averaged 75 mg/L with a maximum concentration of 82 mg/L. Figure 5-9 presents a graph of disappearance of the influent 2,4-DNT and appearance of effluent DAT.

The AnFBR reduced influent alcohol concentrations to non-detectable levels. Acetate concentrations in the effluent averaged 9 mg/L. The COD feed was reduced from 800 mg/L to an average of 330 mg/L. Ether (approximately 40 mg/L) again passed through the system without reduction.

Because all of the measurements of 2,4-DNT concentrations in the AnFBR and RBC effluent samples were either below detection (i.e., <0.10 mg/L) or less than twice the detection limit, it is assumed that the difference indicated in the table is due to analytical variability at these low levels.

Gas flow rates of up to 34 L/hr were recorded. The methane concentration in the reactor offgas averaged 85 percent. Carbon dioxide was not detected.

The RBC degraded approximately 67 percent of the DAT present in the AnFBR. It degraded all the alcohol, ether, and acetate in the AnFBR effluent. The COD of the RBC effluent was approximately 108 mg/L.
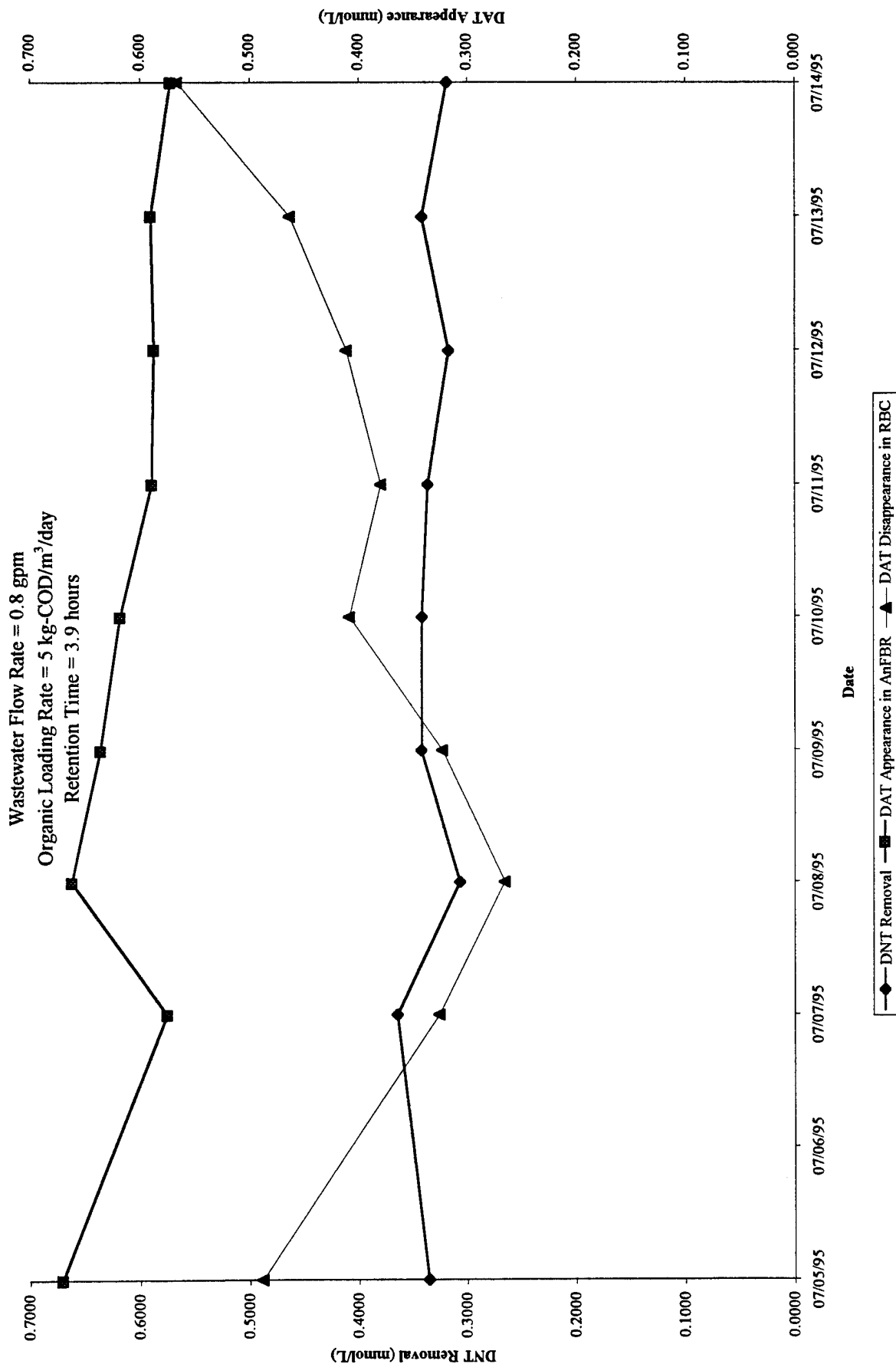
Table 5-11
Analytical Data for Test Run No. 6
July 5, 1995 - July 14, 1995

	AnFBR Influent									AnFBR Effluent							RBC Effluent						
Date	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD*, (mg/L)	Organic Loading Rate (kg-COD/m³/day)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
07/05/95	61.10	<0.10	44	12.6	42	7.0	ND	859.59	5.27	<0.10	81.88	ND	42	9	56	401	<0.10	22.34	ND	ND	3	ND	111
07/06/95	71.79	<0.10	36	12.6	43	7.0	4	523.59	3.21	<0.10	NA	NA	43	10	28		0.1	NA	NA	NA	NA	NA	116
07/07/95	66.34	<0.10	35	12.6	40	4.0	ND	819.59	5.02	<0.10	70.28	ND	41	10	32	316	<0.10	30.59	ND	ND	<2	ND	116
07/08/95	55.87	<0.10	34	12.6	43	7.0	4	815.59	5.00	<0.10	80.82	ND	43	11	34	337	<0.10	48.48	ND	ND	8	4.0	143
07/09/95	62.30	<0.10	33	12.9	43	4.0	ND	831.05	5.09	<0.10	77.64	ND	43	8	29	324	<0.10	38.26	ND	ND	<2	ND	104
07/10/95	62.25	<0.10	33	13.4	43	3.0	ND	840.83	5.15	<0.10	75.43	ND	44	7	36	324	<0.10	25.63	ND	ND	3	ND	107
07/11/95	61.27	<0.10	32	13.4	40	8.0	3	850.83	5.22	<0.10	71.92	ND	42	8	26	318	<0.10	21.54	ND	ND	<2	ND	95
07/12/95	57.68	<0.10	32	12	38	8.0	4	797.65	4.89	<0.10	71.69	ND	39	12	24	356	<0.10	15.59	ND	ND	3	ND	140
07/13/95	62.23	<0.10	31	16	39	6.0	ND	960.87	5.89	<0.10	72.07	ND	40	8	9	304	<0.10	0.79	ND	ND	5	ND	94
07/14/95	58.11	<0.10	30	14.7	37	8.0	4	892.85	5.47	<0.10	69.90	ND	39	9	14	300							64
Average	61.89	<0.10	34	13.3	41	6.2	3.8	819.24	5.02	<0.10	74.63	ND	42	9	29	331	<0.10	25.43	ND	ND	3	ND	108
Maximum	71.79	<0.10	44	16.0	43	8.0	4.0	960.87	5.89	<0.10	81.88	ND	44	12	56	401	<0.10	48.48	ND	ND	8	4.00	143

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

Figure 5-9
DNT Removal and DAT Appearance During Test Run No. 6
July 5, 1995 - July 14, 1995

Wastewater Flow Rate = 0.8 gpm
Organic Loading Rate = 5 kg-COD/m³/day
Retention Time = 3.9 hours

Test Run No. 7

The seventh test run was conducted between July 19 and July 21, 1995 (Table 5-12). The influent flow rate of water-dry wastewater was increased to 1.2 gpm, providing an empty bed hydraulic residence time of 2.6 hours. Supplemental alcohol was fed to the system as during the previous run. The average concentration of 2,4-DNT in the influent was 85 mg/L with a maximum concentration of 93 mg/L. The approximate OLR to the system was 11 kg-COD/m^3/day.

During this operational period, the reactor reduced the influent 2,4-DNT to non-detectable levels. The DAT concentration in the AnFBR effluent averaged 66 mg/L with a maximum concentration of 75 mg/L. Figure 5-10 shows a graph of disappearance of the influent 2,4-DNT and appearance of effluent DAT. The concentrations of both compounds are plotted on a molar basis. As can be seen from this graph, the formation of DAT and the disappearance of 2,4-DNT correlated well.

The influent alcohol was reduced by the system to levels below detection. Acetate in the effluent decreased to an average concentration of 55 mg/L. The COD feed to the system averaged 1,200 mg/L while the average effluent COD was approximately 340 mg/L. Ether, at an average concentration of 19 mg/L, again passed through the system without reduction.

A gas flow rate of up to 58 L/hr was recorded. Methane in the offgas averaged approximately 89 percent. No carbon dioxide was present in the reactor off gas.

Although the RBC removed only 30 percent of the DAT present in the AnFBR effluent, it degraded all of the alcohol, ether, and acetate. The COD of the RBC effluent was approximately 134 mg/L.

Table 5-12

Analytical Data for Test Run No. 7

July 19, 1995 - July 21, 1995

| | AnFBR Influent | | | | | | | | | | AnFBR Effluent | | | | | | | RBC Effluent | | | | | | |
Date	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD *, (mg/L)	Calculated Organic Loading Rate (kg-COD/m³/day)		DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)		DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
07/19/95	76.74	<0.10	271	2.7	23	92	5	1,073.20	9.87		0.03	61.21	ND	33	37	16	298		0.107	18.19	ND	ND	<2	ND	84
07/20/95	85.53	<0.10	349	2.7	17	117	4	1,263.20	11.61		<0.10	62.84	ND	25	73	36	364		<0.10	54.67	ND	<2	4	ND	160
07/21/95	92.64	<0.10	356	2.7	17	119	5	1,290.20	11.86		<0.10	74.74	ND	24	54	37	362		<0.10	63.77	ND	<2	5	ND	157
Average	84.97	<0.10	325	2.7	19	109	5	1208.86	11.11		<0.08	66.26	ND	27	55	30	341		0.10	45.54	ND	<2	4	ND	134
Maximum	92.64	<0.10	356	2.7	23	119	5	1290.20	11.86		<0.10	74.74	ND	33	73	37	364		0.11	63.77	ND	<2	5	ND	160

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampl

Figure 5-10
DNT Removal and DAT Appearance During Test Run No. 7
July 19, 1995 - July 21, 1995

Wastewater Flow Rate = 1.2 gpm
Organic Loading Rate = 11 kg-COD/m³/day
Retention Time = 2.6 hours
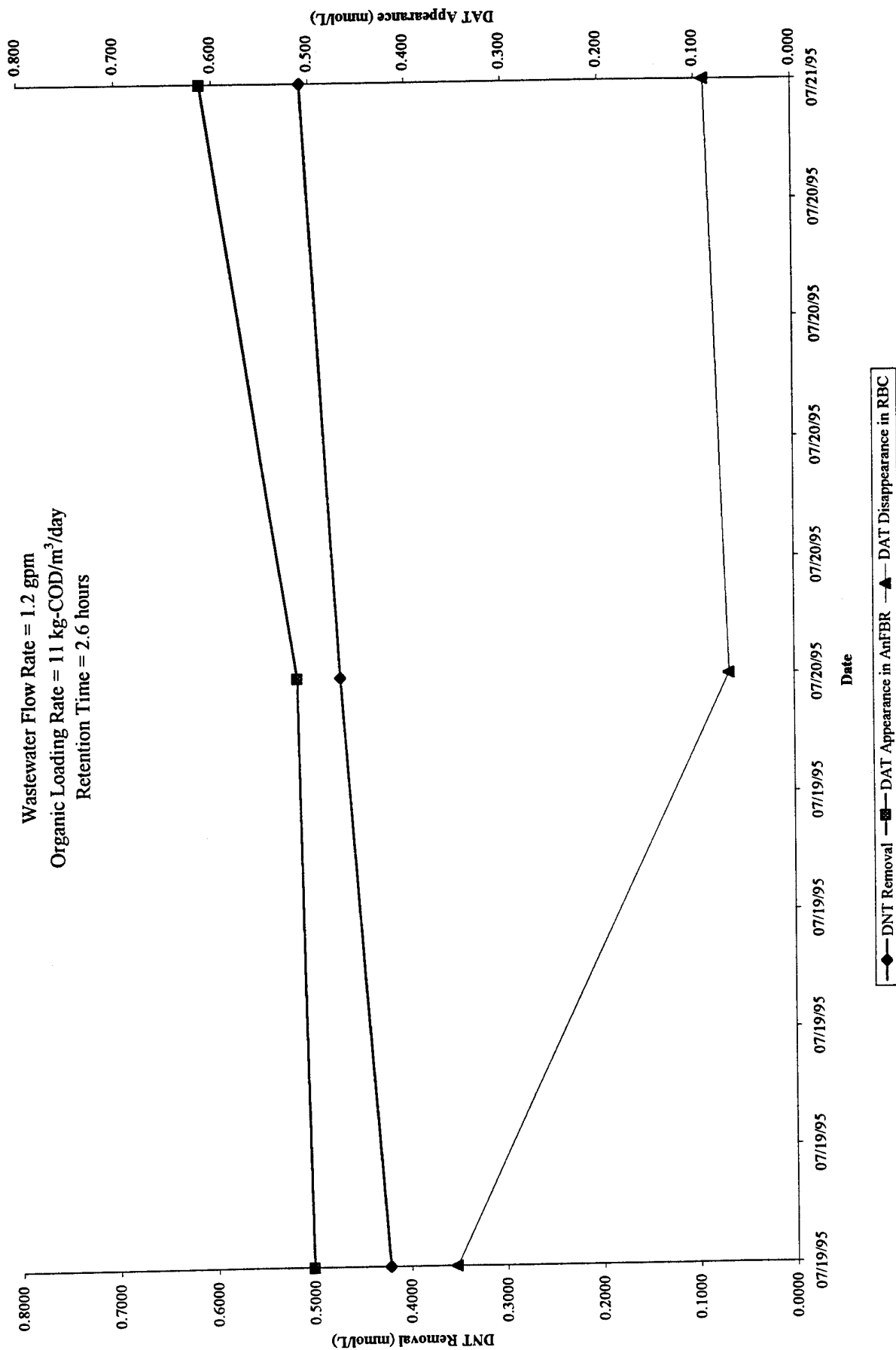
Test Run No. 8

The eighth and final test run was conducted between July 24 and July 26, 1995 (Table 5-13). The forward flow rate of the water-dry wastewater was increased to 2.0 gpm. This rate resulted in an empty bed hydraulic residence time of 1.6 hours. 2,4-DNT averaged 90 mg/L in the untreated wastewater. The maximum concentration measured was 92 mg/L. These conditions resulted in an approximate OLR to the system of about 24 kg-COD/m³/day.

During this operational period, the AnFBR reduced 2,4-DNT to levels below detection. The DAT concentration in the effluent averaged 70 mg/L with a maximum concentration of 80 mg/L. Figure 5-11 shows a graph of achieved reduction of the influent 2,4-DNT and appearance of DAT in the effluent. Alcohol was reduced to an average of 21 mg/L while acetate increased substantially in the effluent to an average of 383 mg/L. The average COD was 1,550 mg/L in the influent and 760 mg/L in the effluent. As observed during all previous runs, ether passed through the system without reduction.

The AnFBR produced gas flow rates of up to 50 L/hr. The methane concentration in the reactor offgas averaged 83 percent. Carbon dioxide was not detected in the offgas.

The RBC did not achieve any reduction of DAT or acetate, however, the alcohol and ether present in the AnFBR effluent were removed. This indicated that the RBC was not acclimated to the increased flow rate and organic loading or that the RBC was undersized. The COD in the RBC effluent was approximately 560 mg/L.

5.6 Evaluation of AnFBR

The results of the AnFBR demonstration indicate that the system is capable of achieving the target effluent quality (i.e., <0.113 mg/L 2,4-DNT). Most of the tests conducted were performed at a relatively low flow rate of 0.4 gpm (i.e., retention time of 7.8 hours). The test runs that were performed at higher flow rates (up to 2 gpm) were run for shortened periods, due to the lack of WD wastewater. Additional testing at flow rates of 4 gpm or higher would enhance the evaluation of the system to achieve the required removal of 2,4-DNT.

Table 5-13
Analytical Data for Test Run No. 8
July 24, 1995 - July 26, 1995

Date	AnFBR Influent										AnFBR Effluent							RBC Effluent						
	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Alcohol Feed, (mL/min)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	Calculated COD*, (mg/L)	Organic Loading Rate (kg-COD/m³/day)		DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)	DNT, (mg/L)	DAT, (mg/L)	Alcohol, (mg/L)	Ether, (mg/L)	Acetic Acid, (mg/L)	Propionic Acid, (mg/L)	COD, (mg/L)
07/24/95	92.36	<0.10	347	15.25	15	118	ND	1,599.47	24.51		<0.10	80.24	4	19	323	65	789	<0.10	78.65	ND	5	228	46	573
07/25/95	89.02	<0.10	351	13.8	16	119	4	1,558.30	23.88		<0.10	64.37	58	19	429	4	811	<0.10	62.62	11	4	404	13	634
07/26/95	89.49	<0.10	353	12.5	15	125	ND	1,514.29	23.20		<0.10	65.13	2	17	397	6	670	<0.10	67.32	ND	3	308	3	484
Average	90.29	<0.10	350	13.85	15	121	4	1,557.35	23.86		<0.10	69.91	21	18	383	25	757	<0.10	69.53	4	4	313	21	564
Maximum	92.36	<0.10	353	15.25	16	125	4	1,599.47	24.51		<0.10	80.24	58	19	429	65	811	<0.10	78.65	11	5	404	46	634

* - Influent CODs are calculated based on the supplemental alcohol feed rate and wastewater COD since the supplemental alcohol addition point was downstream from the influent sampling location.

Figure 5-11

DNT Removal and DAT Appearance During Test Run No. 8

July 24, 1995 - July 26, 1995

Wastewater Flow Rate = 2 gpm

Organic Loading Rate = 24 kg-COD/m³/day

Retention Time = 1.6 hours
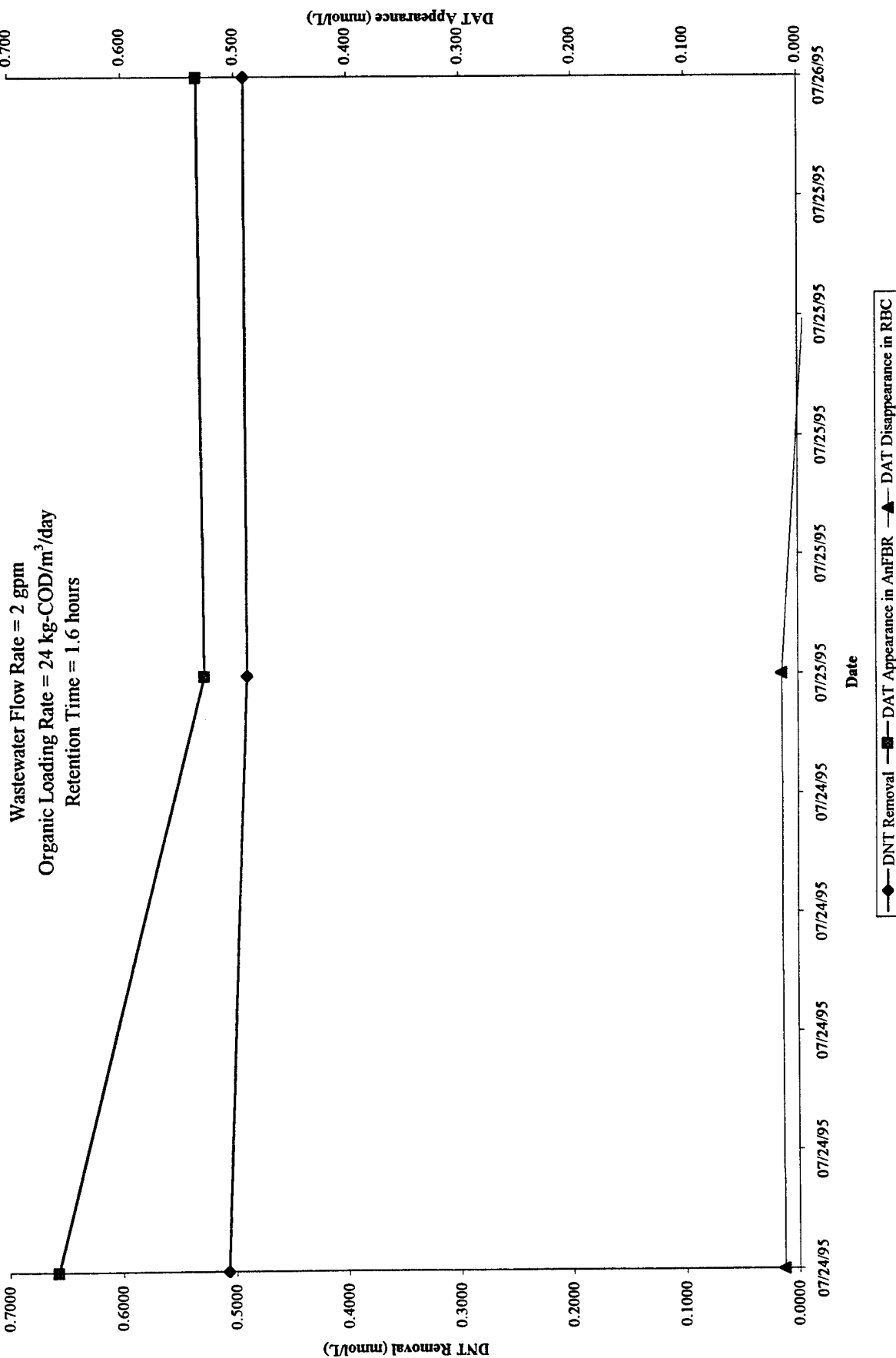
Anaerobic degradation of 2,4-DNT in the AnFBR system results in the formation of 2,4-DAT (Figure 5-12). 2,4-DAT has been shown to be aerobically biodegradable. The pilot-scale RBC reduced 2,4-DAT contained in the AnFBR effluent to levels below detection when allowed to acclimate to increased flow rates and reduced alcohol levels. Thus, the tests indicate the feasibility of aerobic removal of 2,4-DAT by the BWTP. However, the results of the demonstration also indicate that the RBCs in the BWTP may not perform adequately if a substantial portion of the alcohol in the wastewater is removed upstream. Treatment of WD wastewater by AnFBR technology consumes the alcohol and ether present in the wastewater, therefore reducing the loading to the BWTP. The RBCs in the BWTP depend on minimal levels of COD in the wastewater to maintain viable biomass. If the levels drop below minimal requirements, supplemental alcohol must be added. Both the UV/OX and the AnFBR systems reduce alcohol levels in the WD effluent.

AnFBR technology is currently available from a limited number of vendors. Compared with UV/OX, AnFBR is an emerging technology. Because the degree of documented experience with AnFBR is less than with UV/OX, it would likely be more difficult to start up and troubleshoot the AnFBR system. This was evidenced by the startup problems experienced during the demonstrations. Operational upsets were encountered because of complications with the inflow pump, alcohol delivery pump, pH control solution pump, and the main control system. Additionally, level probes in the nutrient and hydrogen peroxide sampling tanks were problematic throughout the study. Although the system, as tested, was computer controlled, the system required significant operator attention. As is typical of biological systems, the AnFBR system required significant time for reacclimation following upsets which can be caused by variation in influent quality, temperature, and other variables.

Figure 5-12

Summary of DNT Removal and DAT Appearance During All Test Runs
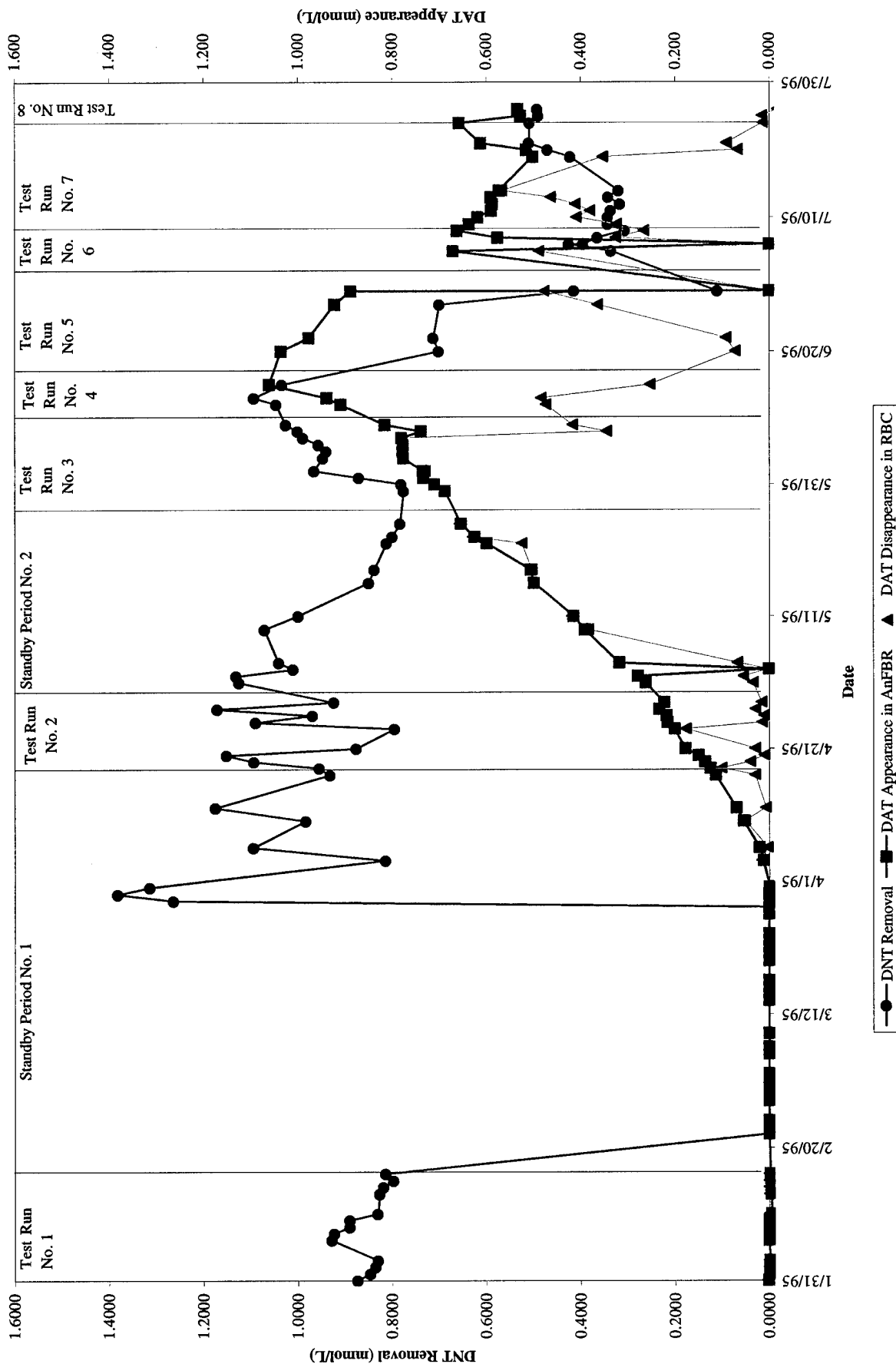
6.0 EVALUATION OF GRANULAR ACTIVATED CARBON

Subsequent to the demonstration of the UV/OX and AnFBR systems, Alliant implemented the use of transportable Granular Activated Carbon (GAC) adsorbers as an interim measure to treat wastewaters generated from the SR and WD operations. This activity was implemented to reduce the 2,4-DNT load to the BWTP so that violations of the NPDES discharge limit for 2,4-DNT would not occur. The data collected during operation of these temporary carbon units was compiled and analyzed in a report submitted to USACERL.[21] The information provided by Alliant is presented here to allow a comparative evaluation of GAC with AnFBR and UV/OX.

6.1 System Description

A trailer mounted, transportable, dual adsorption GAC system (Model No. LPS-2) was acquired by Alliant from Envirotrol, Inc. (Envirotrol), Sewickley, PA on a lease basis. The system consisted of two skid-mounted and pre-piped carbon vessels which were connected in parallel. Each vessel could be loaded with 1,800 lbs of GAC. The system was capable of a maximum flow rate of 100 gpm; however, it was operated at a flow rate of approximately 40 gpm. At this flow rate, the design pressure drop across the system was approximately six pounds per square inch (6 psi).

The GAC system was used to treat effluents from SR (solvent recovery) and WD (water dry) processes. At the time of a scheduled discharge, the system was moved to the appropriate production building and connected directly to the tank to be drained. Wastewater from the tank passed through the GAC which removed 2,4-DNT by adsorption. The treated water was discharged to the industrial sewer system leading to the BWTP. At the conclusion of the draining operation, the GAC system was moved to the next tank scheduled to be drained. Use of this system was initiated in August 1995.

Prior to implementation of the GAC system, a pilot-scale study of GAC treatment of RAAP wastewaters was conducted.[22] This study included treatment of 72,500 gallons of wastewater using two 55-gallon carbon units connected in series. The study was conducted over a period of seven weeks. Based on the results of this study, Alliant concluded that GAC was capable of

removing 2,4-DNT from WD and SR wastewaters. However, the presence of alcohol and ether in these wastewaters inhibited the system's ability to adsorb 2,4-DNT. The GAC system was shown to be capable of achieving the discharge limit of 113 µg/L 2,4-DNT.

During the pilot-scale testing, a carbon loading rate of 0.02 lbs of 2,4-DNT per lb of carbon was observed. In contrast, adsorbance of 2,4-DNT on carbon in the absence of solvents has been reported in published isotherm data to be on the order of 0.2 to 0.4 lbs 2,4-DNT per lb of carbon.[23] Additionally, a previous bench-scale study performed by Alliant had shown that in the presence of solvents, 0.3 lbs of 2,4-DNT per lb of carbon would be adsorbed. Thus, the flow-through pilot-scale study indicated that adsorbance of 2,4-DNT on carbon would be lower than that predicted by the literature and prior bench-scale work. Based on this data, it was estimated that the 3,600 lbs of carbon in the treatment unit could adsorb approximately 72 lbs of 2,4-DNT.

6.2 Data Analysis

GAC system performance data was collected by Alliant for the period between August 30, 1995 and November 14, 1995. Data collected included: influent and effluent concentrations of 2,4-DNT, diaminotoluene (DAT), ethanol, and diethylether; wastewater flow rates and totalized volumes; and influent and effluent pH. With the exception of pH, these data are summarized in Table 6-1. The influent and effluent pH ranged from approximately 6 to 8. There was little difference in the pH of the influent and the effluent and there was no discernible correlation between the pH and other parameters.

The flow totalizer readings presented on Table 6-1 were collected at various intervals of time. The start and end dates reflect the first day after the last flow totalizer reading was taken and the last day before the next reading was taken, respectively. Samples of the influent and effluent were collected during the discharge of each production tank as it was treated in the carbon adsorber; however, the flow totalizer was not read for each of these events. In order to calculate the amount (i.e., pounds) of 2,4-DNT adsorbed on the carbon, it was necessary to calculate an average concentration for all tanks treated.

Table 6-1
Granular Activated Carbon System Operating Data

Start Date	End Date	Wastewater Source	Flow Rate (gpm)	Starting Gallons	Ending Gallons	Total Gallons Water	Average DNT Influent (ppm)	Average DNT Effluent (ppm)	Average Ether Influent (ppm)	Average Ether Effluent (ppm)	Average Alcohol Influent (ppm)	Average Alcohol Effluent (ppm)	Average DAT Influent (ppm)	Average DAT Effluent (ppm)	Pounds of DNT Loaded on Carbon
8/30/95	8/30/95	Solvent Recovery	80	85,292,811	85,305,594	12,783	20.2	<0.1	NA	NA	456.4	45.4	NA	NA	2.14
9/8/95	9/8/95	Solvent Recovery	60	85,305,594	85,308,386	2,792	47.4	0.04	NA	NA	289,906.0	NA	NA	0.03	1.10
9/11/95	9/11/95	Solvent Recovery	55	85,308,386	85,315,032	6,646	27.9	0.01	1,230.5	81.5	24,391.3	11,453.3	4.81	0.00	1.55
9/12/95	9/13/95	Solvent Recovery	55	85,315,032	85,316,094	1,062	2.8	0.01	924.4	851.4	4,578.9	8,832.8	19.80	0.00	0.02
9/14/95	9/14/95	Solvent Recovery	50	85,316,094	85,325,884	9,790	21.5	0.03	330.2	751.8	904.0	7,461.2	45.71	0.00	1.75
9/15/95	9/15/95	Water Dry	40	85,325,884	85,327,181	1,297	51.7	0.10	57.0	363.0	60.3	2,151.0	0.02	0.00	0.56
9/21/95	9/21/95	Water Dry	40	85,327,181	85,336,784	9,603	54.8	0.01	33.5	186.0	36.0	149.3	0.06	0.00	4.38
9/25/95	9/26/95	Water Dry	40	85,336,784	85,365,455	28,671	14.1	0.00	222.8	140.1	229.2	350.9	0.16	0.00	3.37
9/28/95	9/29/95	Solvent Recovery/Water Dry	40	85,365,455	85,373,046	7,591	25.4	0.02	210.7	114.7	311.7	515.7	0.05	0.00	1.61
9/29/95	10/2/95	Solvent Recovery	40	85,373,046	85,382,906	9,860	22.2	0.00	632.0	151.8	11,285.4	1,494.6	1.71	0.00	1.82
10/3/95	10/3/95	Solvent Recovery	40	85,382,906	85,384,850	1,944	11.8	0.02	2,758.6	167.6	2,324.8	2,086.6	5.59	0.00	0.19
10/4/95	10/4/95	Solvent Recovery/Water Dry	40	85,384,850	85,417,041	62,191	23.4	0.03	975.3	1,036.0	6,269.5	3,255.5	1.66	0.01	12.13
10/5/95	10/12/95	Solvent Recovery	40	85,447,041	85,468,475	21,434	25.9	0.01	1,169.9	549.1	1,720.6	1,990.0	2.47	0.09	4.62
10/16/95	10/19/95	Solvent Recovery	40	85,468,475	85,472,085	3,610	11.3	0.02	431.0	415.5	2,291.2	1,330.5	1.32	0.06	0.34
10/20/95	10/23/95	Solvent Recovery	40	85,472,085	85,498,790	26,705	19.3	0.02	985.4	943.8	983.2	4,741.9	0.54	0.11	4.28
10/31/95	11/13/95	Solvent Recovery/Water Dry	40	85,498,790	85,554,180	55,390	24.8	0.01	327.3	408.3	338.4	2,269.6	0.87	0.07	11.44
TOTAL						261,369									51.31
AVERAGE			46			16,336	25.28	0.02	734.89	440.05	21,630.43	3,208.55	6.05	0.02	
MAXIMUM			80			62,191	55	0	2,759	1,036	289,906	11,453	46	0	

Detection Limit for DNT and DAT is 0.02 ppm, for solvents 1.0 ppm.

The average influent concentrations were 25 mg/L 2,4-DNT, 735 mg/L diethylether, 21,600 mg/L ethanol, and 6 mg/L DAT. The maximum influent concentrations were 55 mg/L 2,4-DNT, 2,760 mg/L ether, 289,900 mg/L alcohol, and 46 mg/L DAT. The GAC units reduced the concentration of 2,4-DNT to an average of 0.02 mg/L in the effluent. This treated concentration is significantly less than the NPDES limit of 0.113 mg/L. The highest concentration of 2,4-DNT measured in the effluent (0.1 mg/L) also met the target discharge limit. During the time frame evaluated, a total of 260,000 gallons of SR and WD effluent were treated. It is calculated that the GAC had adsorbed an estimated 51 lbs of 2,4-DNT. This amount is less than the projected capacity of the carbon (i.e., 72 lbs). Therefore, the holding capacity of the carbon was not exhausted during the study period.

The data indicate that the GAC initially adsorbed high levels of both alcohol and ether. These solvents were then desorbed when the influent concentrations dropped. This is evidenced by the fact that the observed concentrations of alcohol and ether in the effluent were frequently higher than the corresponding influent concentrations. However, the data does not indicate that 2,4-DNT or DAT adsorbed on the carbon was resolubilized during period of desorption of these solvents.

Unanticipated concentrations of DAT were occasionally observed in the untreated SR and WD effluent during this period. The DAT was adsorbed on the carbon and reduced to an average concentration of 0.02 mg/L in the effluent.

The system operated largely without problem. However, concerns existed regarding freezes that might occur during its use in winter months. A heater or heat jacket of some type would likely be required as a system modification to allow continual use of the GAC in sub-freezing temperatures.

7.0 ECONOMIC EVALUATION OF ALTERNATIVES

Selection of the most appropriate treatment alternatives must be based first on the ability of the system to remove 2,4-DNT from WD wastewater. Pretreatment of WD wastewater for removal of 2,4-DNT was assumed to be adequate for the RAAP BWTP to treat the whole plant effluent (i.e., wastewater generated from the WD, SR, WS, and CO operations) to the appropriate discharge level. Each of the systems evaluated were demonstrated to be capable of achieving this performance goal. Another critical criteria is cost. To facilitate comparison, an economic evaluation of full-scale UV/OX, AnFBR, and GAC systems for pretreating the WD wastewater at the RAAP is presented in this section. The design basis, the required full-scale flow rate and anticipated 2,4-DNT concentration, and the assumptions used in preparing the design basis are specified below. The selection of full scale equipment is then discussed for each technology. Finally, an economic comparison of the three technologies is made on the basis of a ten-year life cycle cost analysis and a present worth analysis. Equipment costs for full-scale systems were obtained from the vendors involved in the pilot-scale study. Similar systems are offered by other vendors whose costs may be different. Additional capital costs associated with each system include installation, piping, a surge tank, and electrical connections. These costs have been assumed to be the same for all three technologies and have not been included in the life-cycle cost comparisons.

7.1 Design Basis

Section and sizing of wastewater treatment systems are dependent upon the generation schedule flow rate and composition of the wastewater to be treated. An estimated design basis for a full-scale pre-treatment system to treat WD wastewater was established during the project.[24] This design basis was based on the assumption that production levels of DNT-based propellants (i.e., M6+2, M14/M865, M14/M831A1 and M1 MP) will remain relatively constant at 3.5 to 4.0 million pounds per year over the next three to five years. This production level is consistent with the quantity of propellant manufactured at RAAP during 1995. The available data indicate that

approximately 200 gallons of WD wastewater are generated per 1,000 lbs of propellant produced.[4] Therefore, production of 4 million pounds of propellant per year will generate approximately 800,000 gallons of WD wastewater annually.

Currently, there are eight active WD buildings at RAAP. It is not anticipated that any of the inactive (standby) WD buildings will be reactivated in the future. Each active WD building can process 40,000 pounds of propellant per cycle. A cycle time of 11 to 14 days in WD is typical. At the completion of each cycle, each building discharges approximately 8,000 gallons of WD wastewater. An estimate of the maximum potential WD discharge rate can be made by assuming that all active WD buildings are operated on the same production schedule and that the wastewater from all 16 tanks (two water-dry tanks in each building) is discharged simultaneously. In this case, 64,000 gallons of WD wastewater would be discharged to the industrial sewer. While the likelihood of simultaneous discharge of all WD tanks is remote, and may not be feasible due to physical constraints and staffing levels, it has been used to set the maximum flow event. This volume is, therefore, the maximum surge capacity required for a pre-treatment system.

To determine the design flow rate for a pretreatment system, the flow rate required to treat the maximum WD discharge was calculated. The maximum WD discharge scenario would be encountered if all WD tanks were operated on simultaneous schedules and at the shortest production cycle time. At the shortest production cycle time for DNT propellants of 11 days, the pre-treatment system would be required to treat wastewater at a minimum flow rate of 4 gpm (continuously) in order to treat 64,000 gallons of WD wastewater prior to the next maximum flow event 11 days later. Thus, a single pre-treatment system, capable of processing 4 gpm, is required for full-scale processing of WD wastewater. It is assumed that a pretreatment system would be located in close proximity to the active WD buildings and that the WD tanks would be piped directly to the pretreatment system to avoid contamination or dilution by other effluents. (Design and siting for the full-scale system was not included in the scope of the current demonstrations.)

Propellant production schedules at RAAP are dictated by the timing of orders placed by the U.S. military and by the delivery schedules specified in the orders. The most intensive propellant production schedule, in terms of WD wastewater generation, would involve a production campaign during which all eight active WD buildings would be operated simultaneously. Under this production scenario, the estimated total annual WD wastewater generation of 800,000 gallons would be generated over a period of 138 to 175 days (based on 11 and 14 day cycle times, respectively). Under a second scenario, propellant production would not be continuous and WD effluent would be generated periodically, with periods of days, weeks or months between WD discharges. Therefore, the treatment system must be sized to allow treatment of continuous flow at the maximum rate (i.e., approximately 4 gpm) but must also be capable of operating at significantly lower rates and being taken off-line during extended periods if propellant production is interrupted.

Table 7-1 presents a summary of the influent concentrations of 2,4-DNT observed in the WD wastewater during the demonstrations of the UV/OX and AnFBR systems and also during the more recent operation of the GAC unit by Alliant. As evidenced by these data, 2,4-DNT concentrations in WD wastewater vary widely. A minimum concentration of 2.8 mg/L 2,4-DNT and a maximum of 251.5 mg/L were measured during the demonstrations. The concentration of 2,4-DNT in WD wastewater is dependent on a number of factors including the length of time the propellant remains in the WD tank. The longer the propellant is allowed to remain in a WD tank, the more alcohol is removed by evaporation from the propellant and the WD wastewater. This reduces the solubility of 2,4-DNT in water and some dissolved 2,4-DNT in the WD wastewater precipitates back onto the propellant. This occurrence is enhanced if the heat to the WD tank is turned off, as is frequently done at the end of a cycle. Thus, the longer the propellant remains in the WD tank, the lower is the concentration of 2,4-DNT in the WD effluent. The wide variation in concentrations shown in Table 7-1 are likely to be a result of wastewater being discharged from different WD tanks at different times in the processing cycle.

During the AnFBR demonstration, WD tanks were sometimes discharged prematurely and then refilled so that WD wastewater would be available for the demonstration. Therefore, the concentrations observed during this demonstration could represent the high end of the expected

Table7-1
Range of Influent DNT Concentrations
Experienced During Pilot-Test Demonstrations

	DNT Concentration (mg/L)				Alcohol Concentration (mg/L)			
	AnFBR Demonstration	UV/Oxidation Demonstration	GAC System Use	Overall	AnFBR Demonstration	UV/Oxidation Demonstration	GAC System Use	Overall
Average	146.81	90.59	25.28	87.56	192.44	298.05	21,630.43	7,373.64
Maximum	251.50	123.67	54.77	251.50	654	964.33	289,906	289,906
Minimum	20	59.90	2.80	2.80	30	93.33	36	30
Standard Deviation	51.66	27.43	14.52	64.39	142.53	276.18	71,813.61	28,084.78

range of concentrations. During the demonstration of the UV/OX system, wastewater was obtained from routine propellant manufacturing operations and no attempts were made to discharge WD tanks early. The average concentration of 90 mg/L 2,4-DNT observed during these tests may be more representative of normal operations. During Alliant's recent use of the GAC system, mixed wastewaters were treated including wastewater from SR which had lower 2,4-DNT concentrations than WD wastewater. The average concentration of all data points available regarding WD characterization indicate that 100 mg/L 2,4-DNT is the approximate average in WD effluent. This is similar to the concentrations observed during the UV/OX demonstration and has been used as the design concentration for estimating the size of a full-scale system.

The concentrations of ethanol measured in WD effluent during the demonstrations of the UV/OX and AnFBR systems and during operation of the GAC are also presented in Table 7-1. The concentration of ethanol in WD effluent varied more widely than did the concentrations of 2,4-DNT. As with 2,4-DNT, the average concentration of ethanol observed during the UV/OX demonstration have been assumed to be representative of routine operation. Therefore an average of 300 mg/L ethanol was used in the design basis.

7.2 Economic Analysis for UV/OX System

As discussed in Section 4, the destruction of 2,4-DNT by the UV/OX system was impacted by the concentration of alcohol present in the WD wastewater because the alcohol competes for the oxidizing radicals. During the final test run (Test No. 9), the UV/OX system reduced an influent concentration of 60 mg/L 2,4-DNT to levels below the NPDES effluent limit of 0.113 mg/L. During this test the influent contained approximately 300 mg/L ethanol. A residence time of 480 minutes was required to achieve this destruction efficiency. The concentration of 2,4-DNT in the WD wastewater during this test run (60 mg/L) was somewhat lower than the design basis (100 mg/L 2,4-DNT). These results indicate that after 480 minutes of treatment, the alcohol was destroyed and therefore would not interfere with treatment of the remaining 2,4-DNT if the residence time was extended. For the purpose of design basis, a UV/OX system capable of providing a residence time of 960 minutes, twice that used in Test No. 9, was selected for the

full-scale system. At a wastewater flow rate of 4 gpm, a reactor volume of approximately 3,900 gallons would be required to achieve this residence time.

In a full-scale application, the UV/OX system would include an ozone generator capable of providing 2,400 mg/L ozone, approximately 115 lbs/day ozone for a 4 gpm system. The system would also include a hydrogen peroxide delivery system capable of delivering 200 mg/L (or about 9.5 lbs/day) hydrogen peroxide. Total lamp power of 55 kW would be required and the total electricity draw of the system would be about 81 kW (including the ozone generator). Cost of electricity at RAAP was assumed to be $0.04 per kW-hr.

To enhance operation and minimize operator time, the UV/OX system should be controlled by a PLC connected to a computer and autodialer that would permit remote access and monitoring of system performance. The autodial feature would alert on-call personnel of changes in system status and would reduce the requirements for continuous monitoring by operators.

The capital cost for the UV/OX system with the controls outlined above is estimated to be about $150,000.[25] Additional capital costs associated with the system would include installation, piping, the 64,000 gallon surge tank, and electrical connections. These costs have been assumed to be the same for all three technologies evaluated and have not been included in the life-cycle cost comparisons. The estimated capital and operating costs for a full-scale UV/OX system are presented in Table 7-2. Operating costs for the system include electrical power, operating labor, hydrogen peroxide, and lamp replacement costs. Electrical requirements include power to operate the lamps, pumps, and ozone generator. The daily power cost for operating the system is estimated to be $78.

Little operator attention was required during the demonstration of the UV/OX system. It has been assumed that an operator would be required 5 percent of the time for operation of a full-scale system. The average annual burdened salary for an operator has been assumed to be $35,000. Therefore, the annual operator costs would be about $1,650 (assuming 175 days of operation).

Table 7-2
Cost Estimate for Full-Scale Operation of an UV/Oxidation Unit

Item	Unit Cost		Number of Units	Total
Fixed Cost				
Capital Cost	$150,000	ea	1	$150,000
Delivery to Site	$5,000	LS	1	$5,000
Total Fixed Cost				**$155,000**
Annual Operating Cost				
Electricity	$78	/day	175	$13,608
Operating Labor	$35,000	/year	0.05	$1,678
Hydrogen Peroxide	$7	/day	175	$1,208
Lamp Replacement Costs	$33	/day	175	$5,775
Total Annual Operating Cost				**$22,269**
Total Costs for First Year's Operation				**$177,269**
Cost Per 1,000 Gallons For One Year Of Operation (Based on 800,000 gallons Annual Volume)				**$222**
Annual Operating Cost Per 1,000 Gallons (Based on 800,000 gallons Annual Volume)				**$28**
Present Value of Operation (10 years at 7%)				**$311,410**
Equivalent Uniform Annual Cost (10 years at 7%)				**$44,338**

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The cost of hydrogen peroxide is estimated to be on the order of $7/day. Lamp replacement costs are estimated to be $33/day based on 175 days of operation. The lamps are rated for 9,000 hours of operation, on average they will require replacement once per year of operation.

The annual operating cost for a full-scale UV/OX system has been estimated to be $22,270 (Table 7-2). Using a 7 percent discount factor and a ten year life cycle, the present value cost for this is system is $311,410.

7.3 Economic Analysis for AnFBR System

As discussed in Section 5.6, the extended startup and acclimation time encountered during the demonstration and the limited volume of WD wastewater available did not permit determination of the maximum treatment capacity of the AnFBR system. The maximum loading rate achieved during the demonstration was 1.4 kg-DNT/m^3/day (during the eighth operational period). Based on the performance of the AnFBR system and the specified design criteria, EFX recommended an Envirex Model 190 system for the full-scale application.[26]

7.3.1 Model 190

The Model 190 is the next larger standard size in relation to the Model 30 that was tested at RAAP and has 5.2 m^3 of working bed volume. The height of the column on this unit is approximately 5 feet more than that of the Model 30. At the design concentration of 100 mg/L 2,4-DNT and design flow rate of 4 gpm, the full-scale system would see a 2,4-DNT loading rate of 0.4 kg-DNT/m^3/day. Based on this 2,4-DNT loading rate and the estimated capacity of the Model 190 to degrade 2,4-DNT, it is estimated that this system would offer a safety factor of 3.5.

In a full-scale application, the Model 190 could be set up in a configuration similar to that used for the pilot-scale demonstration with the exception that the gas measurement and analysis equipment would not be necessary for operation and could be eliminated. A PLC connected to a computer and autodialer would control the system and permit remote access and monitoring of its performance. The autodial system would alert on-call personnel of system needs and status which would reduce the requirements for continuous monitoring by operators.

The current capital cost for a Model 190 with the controls outlined above is estimated to be $225,000.[26]

The estimated capital and operating costs for a Model 190 system are shown in Table 7-3. The operating costs for the system include electrical power, operating labor, supplemental ethanol, nutrients, and GAC (to replace bed loss due to attrition). Electrical costs include power required to operate pumps and heat the influent water. Based on the horsepower of the pumps on the Model 190, power costs for operation of the system is estimated to be $5.00 per day.

Extensive operator intervention was required during the pilot-scale demonstration to keep the AnFBR system operational. Most of this effort was associated with initial startup and debugging of the equipment. However, after the system was operating with some reliability, operator attention was required at least once every other day. It is assumed that a quarter time operator would be necessary to operate a full-scale system. At an average annual burdened salary for an operator at $35,000, the annual operator costs are estimated to be $8,750.

Based on the results of the demonstration, a COD to 2,4-DNT ratio of 3:1 is required for effective management. Using the design basis influent ethanol concentration of 300 mg/L, supplemental COD would not be required. However, because the ethanol concentrations were observed to vary widely, provision of 100 mg/L of supplemental COD as ethanol (33 mg/L ethanol in 4 gpm wastewater) has been included in the cost analysis to provide flexibility in system operation. To meet this need, approximately 0.24 gpd of alcohol would be required.

During periods when WD wastewater is not generated, (i.e., between production runs), supplemental ethanol must be fed to the AnFBR to maintain the viability of the biomass. Based on the results of the demonstration, an OLR of 5 kg-COD/m^3/day should be adequate for this purpose. At 4 gpm wastewater flow, an alcohol flow rate of 8.5 gpd would maintain this OLR. The contract price for ethanol at RAAP is $1.65 per gallon. The cost for ethanol is estimated to be $0.4/day when WD wastewater is available and $14.03 per day when WD wastewater is not available.

Table 7-3
Cost Estimate for Full-Scale Operation of an AnFBR Unit
Model 190

Item	Unit Cost		Number of Units	Total
Fixed Cost				
Capital Cost	$225,000	ea	1	$225,000
Delivery to Site	$1,500	LS	1	$1,500
Total Fixed Cost				**$226,500**
Annual Operating Cost				
Alcohol with Wastewater Feed	$1.65	/gal	42	$70
Alcohol without Wastewater Feed	$1.65	/gal	1,578	$2,605
Operating Labor	$35,000	/year	0.25	$8,750
Nutrients	$2.35	/day	365	$858
Electricity	$4.99	/day	365	$1,821
GAC Replacement Costs	$0.36	/day	365	$131
Total Annual Operating Cost				**$14,235**
Total Costs for First Year's Operation				**$240,735**
Cost Per 1,000 Gallons For One Year Of Operation (Based on 800,000 gallons Annual Volume)				**$301**
Annual Operating Cost Per 1,000 Gallons (Based on 800,000 gallons Annual Volume)				**$18**
Present Value of Operation (10 years at 7%)				**$326,478**
Equivalent Uniform Annual Cost (10 years at 7%)				**$46,483**

The nutrient requirements for a full-scale system were estimated by assuming costs of 1.25 times the current bulk prices listed in the Chemical Marketing Reporter for sodium phosphate and urea, and twice the current bulk price for the trace minerals required. The total cost for nutrients is estimated to be $2.35/day.

Loss of GAC from the system through attrition and carryover has been estimated to be 5 percent annually.[26] The average daily cost for carbon replacement, based on this assumption, is estimated to be $0.36 per day.

The annual operating cost for a full-scale Model 190 AnFBR system is estimated to be $14,330 (Table 7-3). Using a 7 percent discount factor and a 10 year life cycle, the present worth cost for this system is estimated to be $326,480.

7.3.2 Model 70

As possible alternates to the Model 190 system, EFX provided information on both: a custom Model 70 system with a 15-foot tall, 30-inch diameter reactor, and a modified Model 30, utilizing a taller reactor column (28 feet column with a usable bed height of 25.2 feet versus the Model 30 system used in this demonstration which had a standard 15-foot reactor column with a usable bed height of 11.5 feet). The estimated costs of these alternate AnFBR systems were also evaluated for purposes of comparison.

The estimated capital and operating costs for a Model 70 system are shown in Table 7-4. EFX estimated that a Model 70, which has an estimated capital cost of $175,000, would be operated at a recycle flow rate of 67.5 gpm (using a 3 hp pump) to meet the design criteria presented in Section 7.1. In this scenario, the usable COD:DNT ratio would be 6.3:1, which is greater than the 3:1 ratio required for transformation of 2,4-DNT. The Model 70 would not provide a safety factor for degrading 100 μg/L DNT in 4 gpm wastewater flow. To maintain the operational flexibility necessary to respond to varying alcohol concentrations, approximately 0.24 gpd of supplemental alcohol would be required. During standby periods, an OLR of 5 kg COD/m^3/day could be maintained by feeding 2.6 gpd of alcohol into a forward flow of 4 gpm of water. Based

Table 7-4
Cost Estimate for Full-Scale Operation of an AnFBR Unit
Model 70

Item	Unit Cost		Number of Units	Total
Fixed Cost				
Capital Cost	$175,000	ea	1	$175,000
Delivery to Site	$1,500	LS	1	$1,500
Total Fixed Cost				$176,500
Annual Operating Cost				
Alcohol with Wastewater Feed	$1.65	/gal	42	$70
Alcohol without Wastewater Feed	$1.65	/gal	485	$801
Operating Labor	$35,000	/year	0.25	$8,750
Nutrients	$1.19	/day	365	$434
Electricity	$2.15	/day	365	$784
GAC Replacement Costs	$0.11	/day	365	$40
Total Annual Operating Cost				$10,879
Total Costs for First Year's Operation				$187,379
Cost Per 1,000 Gallons For One Year Of Operation (Based on 800,000 gallons Annual Volume)				$234
Annual Operating Cost Per 1,000 Gallons (Based on 800,000 gallons Annual Volume)				$14
Present Value of Operation (10 years at 7%)				$252,912
Equivalent Uniform Annual Cost (10 years at 7%)				$36,009

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on the current contract price of $1.65 per gallon ethanol at RAAP, the cost of ethanol is estimated to be $0.4/day when WD wastewater is generated and $4.29/day during standby.

Due to the smaller bed size of the Model 70, the nutrient requirements would be reduced to approximately $2.26 per day when the system is operating and $0.20 per day during standby periods. Based on 175 operating days per year, this equates to $1.19 per day. The estimated average daily cost for carbon replacement due to GAC attrition and carryover is $0.11. Labor costs for operation of the Model are assumed to be the same as that estimated for the Model 190.

7.3.3 Modified Model 30

Finally, the cost of a modified Model 30 system was estimated to assess the costs of converting the system used for the demonstration to full-scale, permanent use. Modifications to the Model 30 skid necessary to incorporate a taller column are estimated to cost approximately $20,000. All other system components would remain unchanged. Estimated electrical costs for a modified Model 30 would be approximately half that of a Model 70 system.

7.4 Economic Analysis for GAC System

Based on the data collected by Alliant and summarized in Section 6, the ultimate adsorption capacity for 2,4-DNT on GAC could not be determined because break-through of 2,4-DNT did not occur (i.e., the GAC was not exhausted). Therefore, the carbon consumption rate presented in the initial study conducted for Alliant by Envirotrol cannot be refined. The anticipated carbon capacity of 72 lbs of 2,4-DNT per two 1,800 lb adsorbers (0.02 lbs DNT/lb carbon) therefore, has been assumed in this economic analysis.

The capital and operating costs for the GAC system are presented in Table 7-5. The current lease rate of the Envirotrol Model LP-2 unit is $1,800 per month ($21,600 per year).[21] In addition, the cost of filling this unit with 3,600 lbs of carbon is $3,060 ($0.85 per lb).[21] Cost for delivery of the unit to the site is an additional $1,300 and a system demobilization fee of $2,300 will be charged at the termination of the lease.[21] The demobilization fee covers decontamination, reactivation of the spent carbon, and disposal of residuals. Not including the annual lease rate, the initial fixed cost fee of the system is, therefore, $6,660.

Table 7-5
Cost Estimate for Full-Scale Operation of a GAC Unit

Item	Unit Cost		Number of Units	Total
Fixed Cost				
Initial Carbon Cost	$0.85	/lb	3600	$3,060
Delivery to Site	$1,300	LS	1	$1,300
Demobilization Fee	$2,300	LS	1	$2,300
Total Fixed Cost				**$6,660**
Annual Operating Cost				
Lease of Model LPS-2 GAC Units	$1,800	/month	12	$21,600
Changeout Costs	$5,710	/ea	10	$57,100
Electricity	$15	/year	1	$15
Operating Labor	$35,000	/year	0.05	$1,750
Total Annual Operating Cost				**$80,465**
Total Costs for First Year's Operation				**$87,125**
Cost Per 1,000 Gallons For One Year Of Operation (Based on 800,000 gallons Annual Volume)				**$109**
Annual Operating Cost Per 1,000 Gallons (Based on 800,000 gallons Annual Volume)				**$101**
Present Value of Operation (10 years at 7%)				**$571,812**
Equivalent Uniform Annual Cost (10 years at 7%)				**$81,413**

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Changeout of the GAC during the lease term will be provided by Envirotrol at the rate of $5,710 per changeout.[21] This fee includes removal of spent carbon, transportation of the GAC to Envirotrol's facility as a RCRA hazardous waste, reactivation of the GAC, and delivery and installation of 3,600 lbs of virgin GAC in the system.

The electrical cost of operating the GAC unit is minimal. Assuming that the unit would be operated at an average flow rate of 50 gpm, a 1-hp pump would be adequate. At 50 gpm, the pump would operate for approximately 420 hours in a year. Using an assumed cost of $0.04 per kWh, the estimated annual utility cost for operating this system is about $15.

Little operator attention is required to operate the portable GAC system. It is assumed that one operator would be required about 5 percent of the time during the 172 days of system operation.

The average annual burdened salary for an operator is assumed to be $35,000. Therefore, the annual operator costs are estimated to be $1,750.

Based on a concentration of 100 mg/L 2,4-DNT and 300 mg/L alcohol and a volume of 800,000 gallons of wastewater, the quantity of 2,4-DNT that would be removed by the carbon per year would be approximately 670 lbs. The amount of carbon required for this removal is estimated to be 33,500 lbs. At a rate of 72 lbs of 2,4-DNT per 3,600 lbs of carbon, approximately 10 carbon changeouts would be required per year. The associated annual cost would be on the order of $79,000.[26] With the addition of the annual fixed cost of $6,600, the total cost for operating the GAC system for one year would be approximately $85,500.[26] This results in a treatment cost of $107 per 1,000 gallons. Using a 7 percent discount factor, the life cycle cost for this is system is $559,500.

As an alternative to leasing a carbon system, RAAP could opt to purchase a Model LPS-2 carbon adsorption unit. The purchase price for this system, including the initial carbon charge, is approximately $16,000. Although the annual operating cost of a purchased system would not include the lease rate of $1,800 per month it would, however, include a disposal cost for the 10 carbon changeouts required per year. Since 2,4-Dinitrotoluene is a RCRA hazardous material

Table 7-6
Comparison of Cost Estimates for Full-Scale Operation of Treatment Systems
for the Design Basis of 4 Million Pounds of Propellant Production Per Year

	UV/Oxidation	AnFBR		GAC
		Model 190	Model 70	
Fixed Cost	$155,000	$226,500	$176,500	$6,660
Annual Operating Costs	$22,269	$14,235	$10,879	$80,465
Present Value for 10 years at 7%	$311,410	$326,478	$252,912	$571,812
Number of Years	Cumulative Escalated Operating Cost			
	UV/Oxidation	AnFBR		GAC
		Model 190	Model 70	
0	$155,000	$226,500	$176,500	$6,660
1	$177,269	$240,735	$187,379	$87,125
2	$201,097	$255,966	$199,020	$173,223
3	$226,593	$272,263	$211,476	$265,347
4	$253,874	$289,701	$224,803	$363,920
5	$283,065	$308,359	$239,064	$469,393
6	$314,298	$328,324	$254,323	$582,250
7	$347,718	$349,686	$270,650	$703,006
8	$383,478	$372,544	$288,119	$832,215
9	$421,741	$397,002	$306,812	$970,469
10	$462,682	$423,171	$326,813	$1,118,400

(i.e., a listed waste), the cost of carbon regeneration or disposal outside of the current lease agreement may result in a greater operating cost for the purchased system. RAAP has not obtained quotes from Envirotrol to perform this service, therefore, this option was not included in the cost analysis.

7.5 Economic Comparison of Treatment Alternatives

A summary of the cost estimates prepared for each of the three treatment alternatives evaluated in this study is presented in Table 7-6. The present value of each option was calculated based on ten years of operation. An assumed interest rate of 7 percent was used. Calculation of the present value of each alternative takes into consideration the associated capital and operating costs for each alternative and permits direct comparison of the economics of the alternatives. The alternative with the lowest present value based on the stated assumptions is the Model 70 AnFBR system.

The cumulative annual cost of operation of each alternative can also be compared. Table 7-6 shows the cumulative annual operating cost for each alternative from Year 0 (the year the investment in capital equipment is made) through Year 10. The inflation rate for operating costs for each option is assumed to be 7 percent per year. A plot of the cumulative annual cost for the three alternatives is shown in Figure 7-1. Based on this analysis the GAC system has the lowest cumulative cost for the first 2.25 years of operation. Thereafter, the Model 70 AnFBR system has the lowest cumulative cost. The UV/OX system has a lower cumulative cost for the first two years as compared to the AnFBR systems. The Model 190 AnFBR has a lower cumulative than the UV/OX system after approximately seven years of operation.

An analysis was performed to gauge the sensitivity of the economic analysis to the amount of propellant manufactured per year. The same assumptions used for deriving the design basis were used in this analysis (i.e., each WD building can process 40,000 propellants per batch, a typical cycle time is 14 days, and 8,000 gallons of wastewater are generated by each WD building per batch of propellant). The estimated volume of WD wastewater generated per year based on propellant manufacturing rates ranging from 1,000,000 lbs to 6,000,000 lbs per year is shown in Table 7-7. This table also shows the calculated present value of each alternative for ten years of
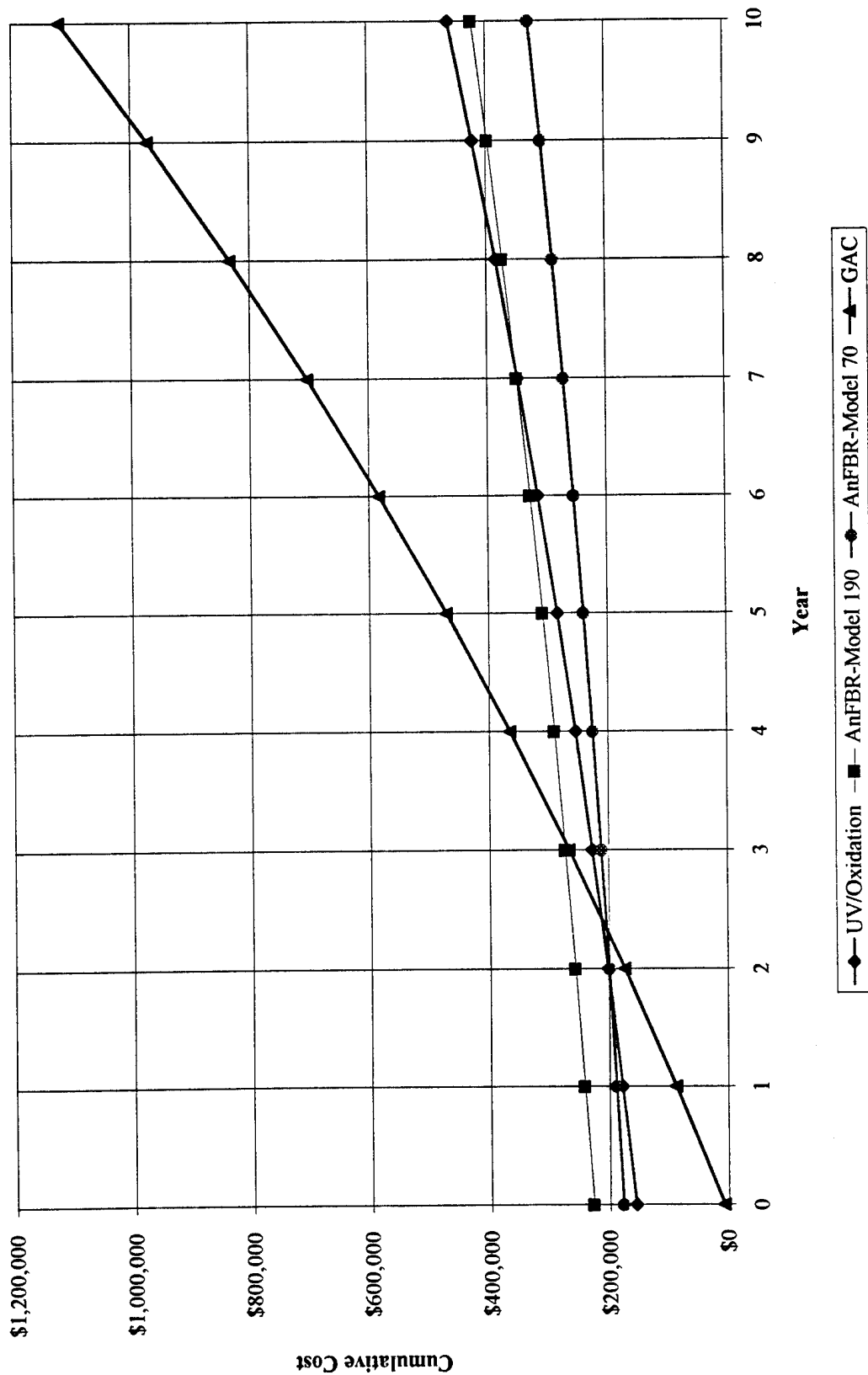
Propellant Manufactured Per Year (lbs)	1,000,000	2,000,000	3,000,000	4,000,000[**]	5,000,000	6,000,000
Wastewater Generated Per Year (gals)	200,000	400,000	600,000	800,000	1,000,000	1,200,000
Number of Days With Wastewater Generation[*]	44	88	131	175	219	263
Capital Costs						
UV/Oxidation	$155,000	$155,000	$155,000	$155,000	$155,000	$155,000
AnFBR - Model 190	$226,500	$226,500	$226,500	$226,500	$226,500	$226,500
AnFBR - Model 70	$176,500	$176,500	$176,500	$176,500	$176,500	$176,500
GAC	$6,660	$6,660	$6,660	$6,660	$6,660	$6,660
Annual Operating Costs						
UV/Oxidation	$5,567	$11,135	$16,702	$22,269	$27,837	$33,404
AnFBR - Model 190	$15,982	$15,399	$14,817	$14,235	$13,652	$13,070
AnFBR - Model 70	$11,110	$11,033	$10,956	$10,879	$10,802	$10,725
GAC	$38,730	$50,150	$61,570	$80,393	$90,120	$101,540
Cost for First Year of Operation						
UV/Oxidation	$160,567	$166,135	$171,702	$177,269	$182,837	$188,404
AnFBR - Model 190	$242,482	$241,899	$241,317	$240,735	$240,152	$239,570
AnFBR - Model 70	$187,610	$187,533	$187,456	$187,379	$187,302	$187,225
GAC	$45,390	$56,810	$68,230	$87,053	$96,780	$108,200
Annual Operating Cost Per 1,000 Gallons						
UV/Oxidation	$28	$28	$28	$28	$28	$28
AnFBR - Model 190	$80	$38	$25	$18	$14	$11
AnFBR - Model 70	$56	$28	$18	$14	$11	$9
GAC	$194	$125	$103	$100	$90	$85
Present Value (10 years at 7%)						
UV/Oxidation	$194,102	$233,205	$272,307	$311,410	$350,512	$389,615
AnFBR - Model 190	$338,748	$334,658	$330,568	$326,478	$322,388	$318,298
AnFBR - Model 70	$254,531	$253,990	$253,450	$252,910	$252,369	$251,829
GAC	$281,735	$364,891	$448,047	$571,307	$654,463	$737,619
Equivalent Uniform Annual Cost (10 years at 7%)						
UV/Oxidation	$27,636	$33,203	$38,770	$44,338	$49,905	$55,472
AnFBR - Model 190	$48,230	$47,648	$47,065	$46,483	$45,901	$45,318
AnFBR - Model 70	$36,239	$36,162	$36,086	$36,009	$35,932	$35,855
GAC	$40,113	$51,952	$63,792	$81,341	$93,181	$105,020

[*] - Based on 8 active water-dry buildings, each capable of processing 40,000 lbs of propellant in a 14 day cycle.

[**] - The design basis condition of 4 million pounds of propellant production per year

Figure 7-1

Ten-Year Life Cycle Cost of UV/Oxidation, AnFBR, and GAC Treatment for the Design Basis of 4 Million Pounds of Propellant Production Per Year

operation and using a 7 percent interest factor. This analysis indicates that UV/OX is the lowest cost alternative for up to 3,000,000 lbs of propellant manufactured per year. Thereafter, the Model 70 AnFBR system is estimated to have the lowest present value cost.

A comparison of the cumulative operating costs over ten years for each alternative at annual propellant manufacture rates of 2,000,000 lbs, 5,000,000 lbs, and 6,000,000 lbs. is presented in Table 7-8. Figures 7-2, 7-3, and 7-4 shows the respective plots of the cumulative annual cost over time for each of the three alternatives. At an annual propellant production rate of 2,000,000 lbs, the GAC system has the lowest cumulative cost for the first 3.5 years of operation (Figure 7-2). Thereafter, the UV/OX system has the lowest cumulative cost.

At an annual propellant manufacture rate of 5,000,000 lbs, the GAC system has the lowest cumulative cost for approximately the first two years of operation (Figure 7-3). Thereafter, the Model 70 AnFBR system has the lowest cumulative cost.

Similarly, as shown in Figure 7-4, at an annual propellant manufacture rate of 6,000,000 lbs, the GAC system has the lowest cumulative cost for approximately the first two years of operation. Thereafter, the Model 70 AnFBR system has the lowest cumulative cost.

Based on the sensitivity analysis presented above, the selection of a system to be implemented at RAAP is dependent on both the amount of propellant likely to be manufactured per year and the length of time that manufacturing rate will be sustained. The difference in operating costs between the UV/OX and AnFBR systems stem primarily from the number of expected operating days per year and is reflective of the fact that the UV/OX system is capable of being shutdown for extended periods of time without the need for operator attention. Thus, the UV/OX system is more cost effective for lower rates of propellant manufacture (i.e., lower volumes of wastewater generated per year). The AnFBR system requires continuous operator attention even in periods when WD wastewater is not generated. Furthermore, the AnFBR system must be fed supplemental alcohol during periods when wastewater is not available to maintain a viable microbial population in the reactor. Thus, increased propellant manufacture rates (and, hence, increased wastewater volumes generated) favor the economics of operation for the AnFBR system.

Table 7-8

Comparison of Cumulative Escalated Operating Costs for 10 Years of Full-Scale Operation

Propellant Manufactured Per Year	2,000,000 lbs				5,000,000 lbs				6,000,000 lbs			
	UV/Oxidation	AnFBR Model 190	Model 70	GAC	UV/Oxidation	AnFBR Model 190	Model 70	GAC	UV/Oxidation	AnFBR Model 190	Model 70	GAC
Fixed Cost	$155,000	$226,500	$176,500	$6,660	$155,000	$226,500	$176,500	$6,660	$155,000	$226,500	$176,500	$6,660
Annual Operating Costs	$11,135	$15,399	$11,033	$50,150	$27,837	$13,652	$10,802	$90,120	$33,404	$13,070	$10,725	$101,540
Present Value for 10 years at 7%	$233,205	$334,658	$253,990	$364,891	$350,512	$322,388	$252,369	$654,463	$389,615	$318,298	$251,829	$737,619

Interest Rate 7.00%

Cumulative Escalated Annual Cost

Number of Years	2,000,000 lbs				5,000,000 lbs				6,000,000 lbs			
	UV/Oxidation	AnFBR Model 190	Model 70	GAC	UV/Oxidation	AnFBR Model 190	Model 70	GAC	UV/Oxidation	AnFBR Model 190	Model 70	GAC
0	$155,000	$226,500	$176,500	$6,660	$155,000	$226,500	$176,500	$6,660	$155,000	$226,500	$176,500	$6,660
1	$166,135	$241,899	$187,533	$56,810	$182,837	$240,152	$187,302	$96,780	$188,404	$239,570	$187,225	$108,200
2	$178,049	$258,376	$199,338	$110,471	$212,622	$254,760	$198,860	$193,208	$224,146	$253,555	$198,701	$216,848
3	$190,797	$276,007	$211,970	$167,887	$244,492	$270,391	$211,228	$296,387	$262,390	$268,518	$210,980	$333,101
4	$204,437	$294,872	$225,485	$229,323	$278,593	$287,115	$224,461	$406,788	$303,311	$284,530	$224,119	$457,492
5	$219,032	$315,057	$239,947	$295,060	$315,081	$305,010	$238,620	$524,917	$347,097	$301,662	$238,177	$590,590
6	$234,649	$336,655	$255,421	$365,398	$354,123	$324,158	$253,770	$651,315	$393,947	$319,993	$253,220	$733,005
7	$251,359	$359,765	$271,979	$440,659	$395,898	$344,647	$269,981	$786,560	$444,078	$339,607	$269,316	$885,389
8	$269,239	$384,493	$289,695	$521,189	$440,597	$366,569	$287,327	$931,273	$497,717	$360,595	$286,538	$1,048,440
9	$288,370	$410,952	$308,652	$607,356	$488,426	$390,026	$305,887	$1,086,116	$555,111	$383,051	$304,966	$1,222,905
10	$308,841	$439,263	$328,935	$699,555	$539,602	$415,125	$325,746	$1,251,798	$616,523	$407,080	$324,683	$1,409,582

Figure 7-2

Cumulative Cost for Treatment of Water Dry Effluent at 2,000,000 lbs Per Year of Propellant Manufacture

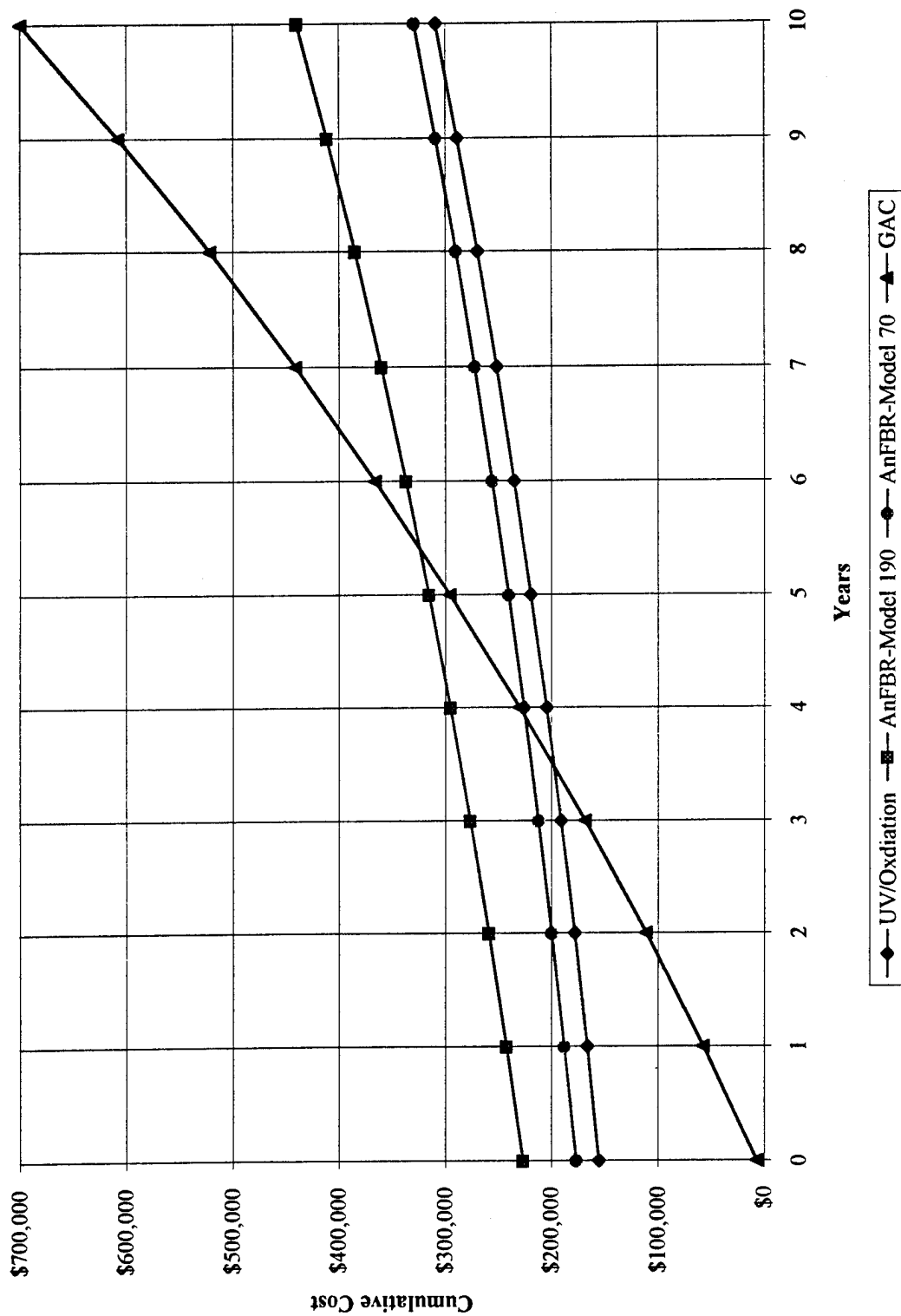UV/Oxdiation ◆ AnFBR-Model 190 ▦ AnFBR-Model 70 ● GAC ▲

Figure 7-3

Cumulative Cost for Treatment of Water Dry Effluent at 5,000,000 lbs Per Year of Propellant
Manufacture

Figure 7-4

Cumulative Cost For Treatment of Water Dry Effluent at 6,000,000 lbs Per Year of Propellant
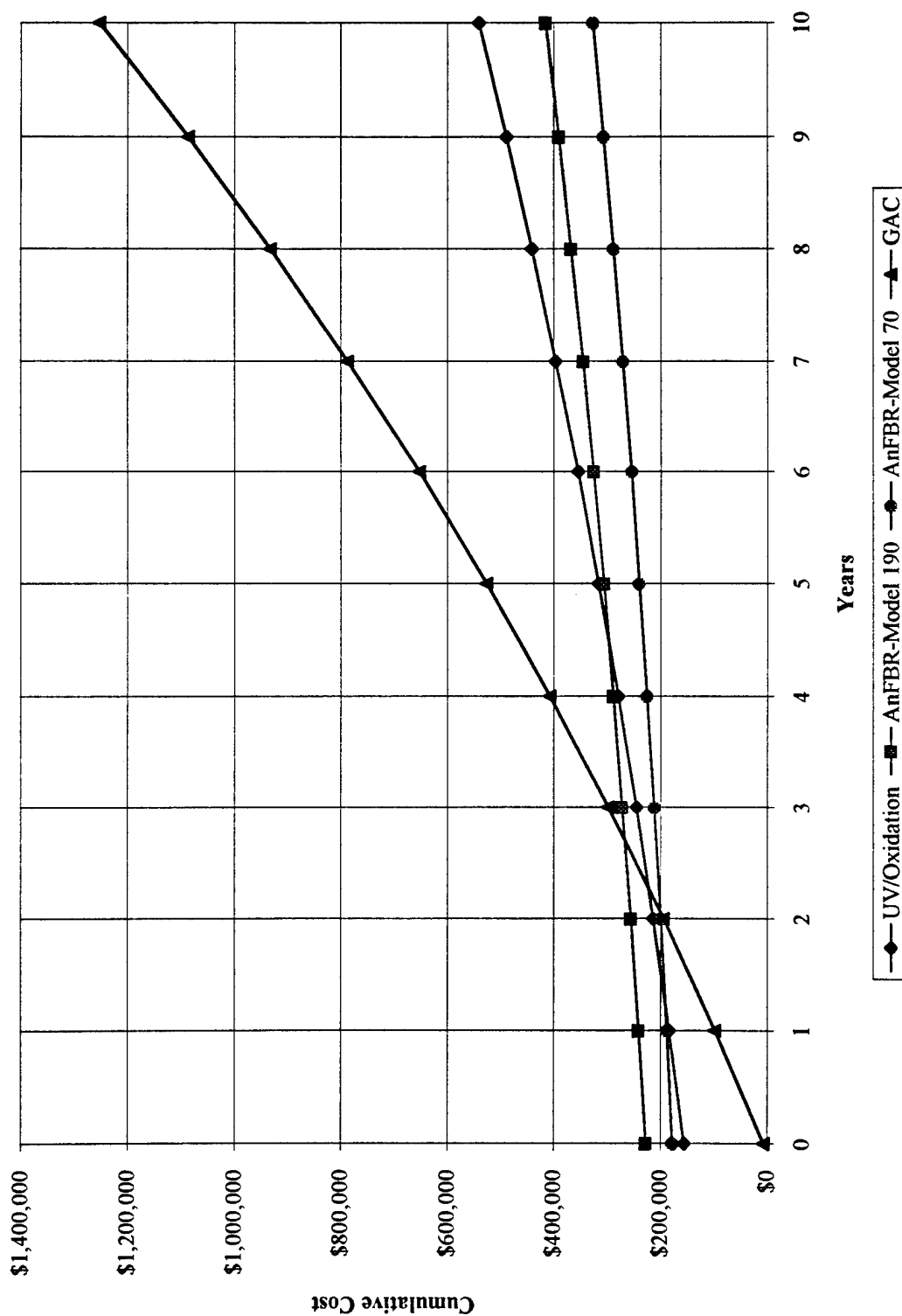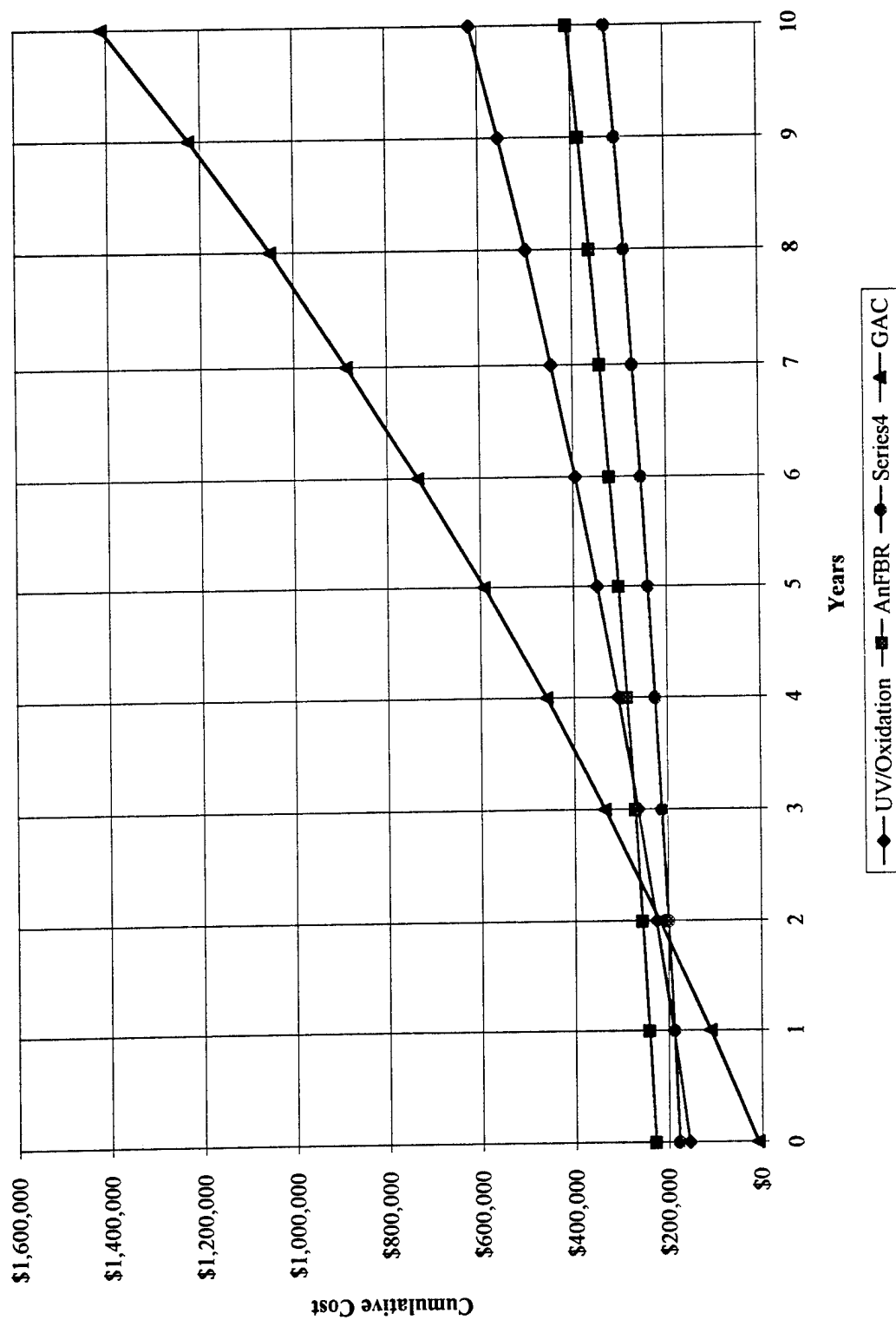Manufacture

8.0 CONCLUSIONS

8.1 System Performance

UV/OX

- The UV/OX system was easily set-up, simple to operate, and required limited operator oversight. It operated without problem during the demonstration period.

- Destruction of 2,4-DNT in WD wastewater can be accomplished by UV/OX, however, the presence of significant concentrations of alcohol and ether necessitates the use of extended retention times.

- During the nine test runs the UV/OX system achieved 2,4-DNT removal rates ranging from 13 to 100%. A combination of H_2O_2 and O_3, in a ratio of 1:3, and a residence time of 480 minutes provided the greatest removal (100%).

- To ensure adequate treatment at full-scale, a UV/OX system should be sized to provide a residence time of 960 minutes and 2,400 mg/L ozone dosage.

- UV/OX technology is well suited for treatment of intermittent flows. The system can be shut down and restarted quickly and as required.

- Wastewater treatment by UV/OX results in effluent with a low pH (<4). Application of a full-scale system will require evaluation of the need for pH adjustment of the treated effluent.

AnFBR

- The AnFBR system required significantly more effort to set up and operate than the UV/OX system. As with any biological system, an acclimation period is required at start-up or after significant changes in operating conditions.

- The system was subject to upsets which were largely associated with equipment problems during initial operations. However, despite these operational upsets the AnFBR consistently reduced concentrations of 2,4-DNT to levels below the target of 0.113 mg/L, and usually below detection, under all test conditions with the exception of Test Run No. 4 when effluent concentrations averaged 0.22 mg/L.

- An AnFBR system would have to be operated continuously to maintain a viable biomass and to avoid lengthy start-up times. Therefore, the system would be operated in recycle mode with supplemental alcohol and nutrients during periods when WD wastewater is not generated.

- DAT formed by the anaerobic degradation of 2,4-DNT in the AnFBR appears to be amenable to aerobic treatment by RBCs.

GAC

- GAC is a proven and readily implementable technology. It has been demonstrated to be effective in removing 2,4-DNT from WD wastewater at RAAP.

- GAC treatment generates carbon which must be regenerated by the vendor or disposed of, usually by incineration. This residual treatment is a significant cost element.

8.2 System Costs

- In a full-scale application, it is estimated that a GAC system will have the lowest cumulative costs (capital investment plus operation and maintenance costs) for the first 2 to 3 years of operation when compared to UV/OX and AnFBR.

- Changes in the concentration of 2,4-DNT present in WD wastewater significantly impact the cost of treatment by GAC.

- Cost estimates presented herein were based on operation to achieve pretreatment levels at or below the NPDES discharge level of 0.113 mg/L for 2,4-DNT. However, pretreatment to higher 2,4-DNT concentrations may be possible as the dilution resulting from mixing pretreated effluent with other non-DNT wastewaters would result in a combined concentration below the limit. In this case, equipment costs for the UV/OX and AnFBR could be reduced (i.e., smaller equipment may be feasible).

- Over longer periods, the UV/OX system is estimated to be the most cost effective at lower propellant production rates (< 2 to 4 million pounds per year) and AnFBR is estimated to have lower cost at higher production rates (> 2 million pounds per year).

8-2

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